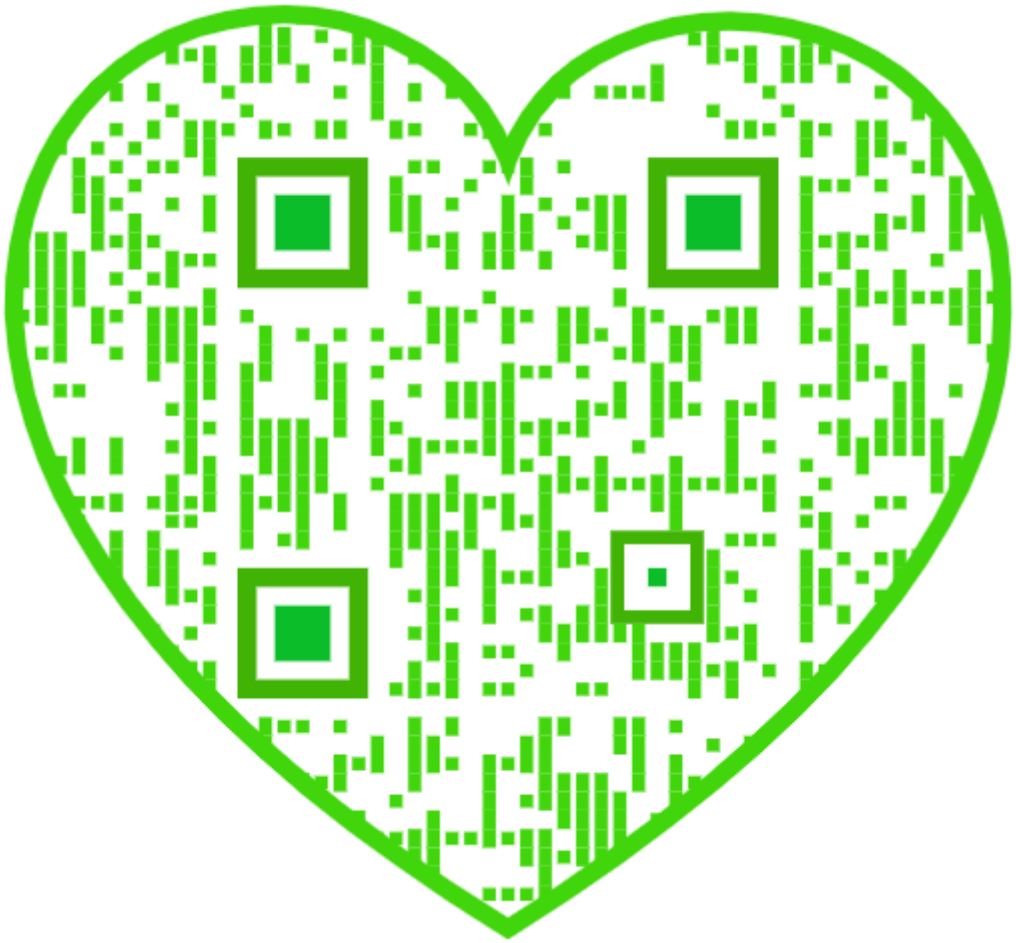

DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, Secretary

UNITED STATES GEOLOGICAL SURVEY
GEORGE OTIS SMITH, Director

Bulletin 625

THE ENRICHMENT OF ORE DEPOSITS

BY

WILLIAM HARVEY EMMONS

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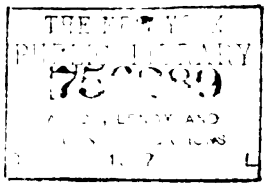

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THE ENRICHMENT OF ORE DEPOSITS.

By William Harvey Emmons.

INTRODUCTION.

STATEMENT OF THEORY.

When mineral deposits are exposed to weathering at and near the surface of the earth, they break down and form soluble salts and minerals that are stable under surface conditions. No metallic sulphide that is long exposed to air and water remains unaltered. Iron sulphides, which are present in practically all sulphide ores, are changed by weathering to iron oxides, and the changes are attended by the liberation of sulphuric acid. Many of the metals form soluble sulphates with sulphuric acid, and when conditions favor their migration downward they are carried in solution to depths where air is excluded. Unoxidized rocks are nearly all alkaline. Acid solutions that encounter such rocks at depths where air is excluded will lose acidity, and as solutions approach a neutral or alkaline condition some of the metals they contain are deposited. When solutions of the metallic sulphates encounter metallic sulphides at depths, precipitation may take place in cracks and fissures, or there may be an interchange between the metals in solution as sulphates and the metallic sulphides. Thus, as a result of precipitation in openings or of chemical interchange, the metals are redeposited, and certain portions of the ore bodies, particularly those just below the oxidizing environment, may be enriched.

In the course of weathering each of the metals behaves in its peculiar way, its behavior depending on its chemical character and relations. Deposits of iron, aluminum, and manganese, and some of gold and other metals, may be enriched near the surface by the removal of valueless materials. On the other hand, many deposits, especially of ores of copper sulphides, are leached near the surface and are much richer below the leached zones. The ore at still greater depths is of lower grade. Without doubt, in a great many deposits the copper leached from the upper zone has been carried downward and redeposited, forming the enriched zone. The deeper, lower-grade sulphide ores are assumed to be representative of the original

or primary material of the whole deposit. Some deposits of gold ores and some of silver ores show similar features. Relatively few deposits of lead and zinc have clearly defined secondary sulphide zones, although some such deposits show appreciable enrichment. The principles involved in the enrichment of ores have become fairly well understood and have proved to be of considerable economic value, for they have been successfully applied to the development of many mineral deposits.

The problems of superficial alteration and enrichment are not simple. Not only do the several metals segregate in different ways, but each metal may behave differently in different mineral associations. Every district and every deposit should be studied separately in the light of all available chemical and geologic data. There are, however, certain laws of segregation that almost invariably are clearly indicated, and as data have accumulated many puzzling apparent exceptions to these laws have disappeared.

This paper is an amplification of an earlier Survey bulletin on the enrichment of sulphide ores (Bulletin 529). It is a discussion of representative deposits, especially of the paragenesis of their ores and of the principles that underlie the processes of enrichment.

I hope it may suggest to those engaged in geologic work and in mining some lines of approach to the solution of the complex problems that are encountered in the field.

I realize fully that there may be serious omissions and possibly errors in the discussion of the complex problems here presented. I shall esteem it a favor if anyone whose statements I may have misquoted or misinterpreted will set me right, and if those who have had superior opportunities for study of certain districts will correct any wrong impressions that I may have given.

DEVELOPMENT OF THEORY.

That rocks and ores are changed near the surface by weathering and that certain metals are in this way segregated was probably known to ancient miners. The earlier geologic literature contains many references to altered outcrops. Superficial changes are in many places conspicuous, and nearly all experienced prospectors, even those without academic training, appreciate fully the significance of gossan and the weathered zone. But the theory that certain metals are dissolved near the surface and precipitated as sulphides below, at, or near a water level is of comparatively recent development. Whitney[1] was probably the first to apply this theory. Describing the deposits of Ducktown, Tenn., in 1854, he said:

[1] Whitney, J. D., The metallic wealth of the United States described and compared with that of other countries, pp. 322–324, Philadelphia, 1854. Also, Remarks on the changes which take place in the structure and composition of mineral veins near the surface, with particular reference to the east Tennessee copper mines: Am. Jour. Sci., 2d ser., vol. 20, pp. 53–57, 1855.

Beneath the gossan is found a bed or mass of black cupriferous ore of variable thickness and width. This, as well as the gossan, is the result of the decomposition of an ore consisting originally of a mixture of the sulphurets of iron and copper which was associated with a quartzose gangue or vein stone. The place of the bed of copper ore marks the limit of the decomposition of the vein; beneath it the ore exists in its original condition. The depth at which the gossan terminates is nearly coincident with the water level or the point where, in sinking, water is found in considerable quantity.

The chalcocite ore Whitney terms "bluish black sulphuret."

Hunt,[1] in 1873, described the Ducktown district, and his conclusions regarding downward changes are essentially like those of Whitney, but he had apparently a clearer conception of the chemistry of the processes of sulphide enrichment. Anticipating by 15 years the experiments of Schuermann, he obviously had in mind a metasomatic interchange of the metals. Said he: "Pyrrhotite is not without action on copper solutions, and its agency has been with great probability suggested * * * as accounting for the precipitation of the copper sulphide."

In the later half of the nineteenth century the theory of so-called "lateral secretion" was widely accepted. The advocates of that theory held that the metals were gathered from rocks near by and precipitated in openings available. A migration of the metals in cold waters was postulated, but the precipitation on older sulphide ore, such as generally takes place in sulphide enrichment, was not assumed to be the prevailing process. In the literature of this period there are, however, numerous references to the migration of the metals in cold solutions from oxidizing ore bodies and to their reprecipitation near by. Becker,[2] in 1882, discussing the paragenesis of ore minerals in the Comstock lode, stated that the rich minerals "have probably formed at the expense of surrounding bodies of lower grade." S. F. Emmons,[3] in his report on Leadville, in 1886, mentioned the migration of silver into country rock. R. C. Hills,[4] describing the Summit district, Colo., in 1883, noted the solution and removal of gold during weathering of kaolinized gold deposits. A noteworthy paper by Penrose[5] on the superficial alteration of ore deposits appeared in 1894. This paper treated the oxidation activities of nearly all the metals separately and greatly stimulated the application of chemical principles to the study of surface decomposition of mineral deposits. The subject of superficial oxidation was

[1] Hunt, T. S., The Ore Knob copper mine and some related deposits: Am. Inst. Min. Eng. Trans., vol. 2, p. 123, 1874.

[2] Becker, G. F., Geology of the Comstock lode and the Washoe district: U. S. Geol. Survey Mon. 3, p. 273, 1882.

[3] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 553, 1886.

[4] Hills, R. C., Ore deposits of Summit district, Rio Grande County, Colo.: Colorado Sci. Soc. Proc., vol. 1, p. 20, 1883.

[5] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 288, 1894.

discussed at some length by Fuchs and De Launay[1] in their treatise published in 1893.

Papers treating the subject of sulphide enrichment were issued in 1900 by S. F. Emmons,[2] W. H. Weed,[3] and C. R. Van Hise.[4] In them the writers, working independently, assembled the geologic and chemical data bearing on the problem, formulating a clearly stated theory from scattered and undigested observations. Five years later Kemp[5] wrote a summary of the processes of secondary enrichment of ore deposits of copper, and in 1910 Ransome[6] issued a comprehensive review of the criteria of downward sulphide enrichment, in which he treated concisely the various processes of enrichment and their results.

DISTINCTIONS BETWEEN PRIMARY AND SECONDARY DEPOSITS.

In the study of mineral deposits it is helpful to outline three groups of processes:

1. The deposition of the deposits.
2. The deformation of the deposits.
3. The superficial alteration and enrichment of the deposits.

Not every ore deposit has been deformed since deposition and not all have been enriched by superficial alteration, but these processes have operated to form or modify a great many deposits. Nearly all geologic processes may, under suitable conditions, operate to form or modify valuable mineral deposits. These, like other geologic bodies, may be deformed by faulting, by folding, by deep-seated metamorphism, or by other processes. Similarly, as rocks are weathered by air and water, so ores are changed, and frequently they are changed more profoundly than rocks, for many ores carry sulphides and these, with air and water, yield sulphuric acid, a very active solvent of many of the metals. When rocks are weathered most of their soluble constituents are carried away and scattered, though some may descend into the earth through openings and be redeposited. The redeposition of certain of the soluble constituents of sulphide ores is very common. In deposits of some metals, in copper deposits, for example, such redeposition is almost though not quite universal. Nearly all the richest deposits of such metals are

[1] Fuchs, Edmond, and De Launay, Louis, Traité des gîtes minéraux et métallifères, vol. 2, p. 230, 1893.

[2] Emmons, S. F., The secondary enrichment of ore deposits: Am. Inst. Min. Eng. Trans., vol. 30, pp. 177–217, 1901.

[3] Weed, W. H., The enrichment of gold and silver veins: Am. Inst. Min. Eng. Trans., vol. 30, pp. 424–448, 1901.

[4] Van Hise, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng. Trans., vol. 30, pp. 27–177, 1901.

[5] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, pp. 11–25, 1906.

[6] Ransome, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 205, 1910.

due to redeposition. Other metals are less soluble; for example, gold dissolves with great difficulty and is likely to be carried away with the débris of its associated minerals. Many of the rich deposits of gold are primary.

In this paper I apply the term "primary" to all bodies of ores whose chemical and mineral composition has remained essentially unchanged by superficial agencies since the ores were deposited. These include ores that have replaced the wall rock and are "secondary" after rock-making minerals or sedimentary beds. A secondary ore, as the term is here used, is one that has been altered by superficial agencies. The term is not restricted to pseudomorphous replacements but is used to include also material deposited by superficial processes in fractures in and near the primary ore bodies. Frequently during the primary deposition of lode ores the veins already formed by ascending waters are fractured, and ascending waters again deposit material in the fractures. Such material, although it is later than the ore first deposited, is not to be regarded as "secondary," for only rarely is it formed by the solution and redeposition of an earlier ore, and its genesis is essentially similar to that of ore of the period of the earliest deposition. A few investigators, however, use the term "secondary" to describe such a deposit and some to describe an ore body formed by ascending solutions that replaced the wall rock. It is unfortunate that the term "secondary" is used with different meanings, but since nearly all writers employ it only to describe the results of downward-moving meteoric waters, reacting in or near an older mineral deposit, I have so restricted its use in this paper. Where the meaning is doubtful I have attempted to avoid ambiguity by using qualifying phrases.

A discussion of the genesis of primary ore deposits does not come within the scope of this paper, but in order to distinguish clearly between primary and secondary ores as the terms are here used, it is desirable to mention briefly the several classes of primary deposits. Any attempt to classify ore deposits by means of the data now available is hazardous. Sharp divisions are not generally found in nature, and any classification based on genesis should be regarded merely as a convenient means of comparison and study. Not only do some classes of primary ores overlap one another, but some primary ores formed at moderate depths by cold solution and some formed very near the surface by ascending thermal waters are in many respects similar to deposits formed by descending sulphate solutions in processes of secondary alteration, and it is not everywhere practicable to draw sharp distinctions between them. The following classification includes the more important groups of primary ores:

Syngenetic deposits; contemporaneous with the inclosing rocks:
- Sedimentary deposits; mechanical, chemical, organic, etc.
- Magmatic segregations; consolidated from molten magmas.

Epigenetic deposits; deposited later than the inclosing rocks:
- Pegmatite veins; deposited by "aqueo-igneous" magmatic solutions.
- Contact-metamorphic deposits; deposited in intruded rocks by fluids passing from consolidating intruding rocks.
- Deposits of the deep-vein zone; formed at high temperature and under great pressure, generally in and along fissures.
- Deposits formed at moderate and shallow depths by ascending hot solutions.
- Deposits formed at and near the surface by ascending hot solutions.
- Deposits formed at moderate and shallow depths by cold meteoric solutions.

The deposits of any of these groups may be changed by various geologic processes. They may be deeply buried and altered by dynamic metamorphism, or they may be folded in the zone of combined fracture and flow, or they may be folded, fractured, or faulted near the surface. Either before or after deformation they may be exposed to weathering and be leached or enriched by superficial processes.

Syngenetic deposits are those that are contemporaneous with the inclosing rocks. Syngenetic deposits include sedimentary beds and magmatic segregations. Sedimentary beds are of course younger than the rocks stratigraphically below and older than the overlying rocks. Sedimentary beds are the sources of many economic products—such as coal, clay, oil, iron ore, or manganese. Of the sulphide ores, however, very few are sedimentary. Some copper deposits in the "Red Beds" have been considered sedimentary—for example the "Kupferschiefer" of Mansfeld, Germany. Workable sulphide deposits of sedimentary origin in the United States are unknown to me.

Magmatic segregations are products of the differentiation of igneous magmas. Genetically considered they are in the strict sense igneous rocks. These deposits include ore bodies of considerable economic importance, among them some of the magnetic iron ores of the Adirondack Mountains, in New York. No large sulphide deposits of this kind are known in the United States. The nickel-copper deposits of Sudbury, Ontario, are the best-known examples of this group in North America. These deposits have been planed off by glacial erosion in recent geologic time and do not show any considerable enrichment by superficial processes.

Pegmatite veins are very nearly related to magmatic segregations. They are magmatic segregations or end products of crystallization that have been thrust, like igneous dikes, into openings in rocks already consolidated. As they are probably formed from eutectic solutions, many pegmatite veins tend to approach a fairly uniform composition and are also generally characterized by large crystals of rock-making minerals. Pegmatites that have not moved from the parent magma and are not related to openings in rocks could properly

be classed with syngenetic deposits, as magmatic segregations, but some authorities reserve the latter term for the more basic differentiation products. In pegmatites the sulphides are present, as a rule, in small quantities, and except some deposits of rare elements they have very little economic importance as sources of the metals.

Contact-metamorphic deposits are formed in intruded rocks by fluids given off by intruding igneous magmas. Many of the ores of such deposits contain the sulphides of copper, zinc, and lead, intergrown with heavy silicates and calcite. In general the ore bodies of this class are not clearly related to determinable fissures. Many of these deposits have been enriched by superficial alteration. As a rule the changes are easily followed in the field, for many minerals that are formed by contact-metamorphic processes are not formed by processes of superficial alteration, and vice versa. In general sulphide enrichment does not extend to great depths in contact-metamorphic ores; the tough, fibrous, or platy minerals of the gangue do not favor extensive fracturing, and the presence of calcite favors precipitation of secondary carbonates near the surface. Exceptions to this rule are known.

The deposits of the deep-vein zone are mineralogically related, more or less closely, to contact-metamorphic deposits. They have formed in and along openings in rocks, however, and in the main they approach the tabular form more closely than the contact-metamorphic deposits. As pointed out by Lindgren, who first defined the group, the deposits of the deeper zone have formed under conditions of high temperature and pressure, which prevail also in contact metamorphism. Because high temperature and pressure are necessary for their genesis these deposits do not form at moderate or shallow depths, at least not in fissures that extend to the surface, and therefore they are seldom found in the more recent rocks. The deposits of this group are closely affiliated with the contact-metamorphic deposits on the one hand and with deposits formed at moderate depth on the other and can not be sharply divided from the latter. If this class is made to include only deposits that are related to openings in rocks and that carry in the gangue some of the contact-metamorphic minerals (such as heavy silicates, magnetite, or specularite), it may be said that the examples found in the United States are but little affected by sulphide enrichment. The gold deposits of this group are generally not manganiferous, and silver is not an important constituent of most of them. On the other hand, some important sulphide deposits of copper that carry pyrrhotite and magnetite might be included in this group, and sulphide enrichment has played an important part in the genesis of a number of these pyrrhotitic copper deposits.

The deposits formed at moderate and shallow depths by ascending thermal solutions constitute a very important group, which includes numerous deposits of ores of copper, gold, silver, lead, and zinc. Many of these deposits show important sulphide enrichment and illustrate the downward migration of the metals. Some of them are noted for relatively small bodies of very rich ore, locally developed in a larger lower-grade deposit. This group, more than any other, may be characterized as the "bonanza" group. Some of the bonanzas are due to sulphide enrichment, but doubtless many of them are primary.

Much may be said for the theory that some of the metals are precipitated most effectively from ascending thermal alkaline solutions in the zone where they first encounter descending ground water. Whether the solutions are alkali chlorides, alkali sulphides, or alkali carbonates, a decrease in temperature and partial oxidation would cause precipitation. An alkali sulphide solution containing iron would be converted to a ferrous sulphate solution, and from such a solution gold would be deposited almost completely. Some of the metals may be precipitated from alkali sulphide solutions merely by dilution. In the deposits of this group, more than in any other, the presence of bonanza ore has little genetic significance. Each deposit and each ore shoot is a separate problem. Even its relation to the present surface is not everywhere conclusive, for obviously the primary bonanza may have a genetic relation to a former zone of ground water—a zone which is itself superficial but which may not be determinable.

Deposits of sulphide ores formed at or very near the surface by ascending hot solutions are mainly of scientific rather than economic importance, although a few of them have been exploited for the metals. As atmospheric oxygen is present in the superficial zone the minerals they contain include the hydrous oxides and various sulphates, and as the pressure is nearly atmospheric the temperature can not have been much above 100° C. Consequently the minerals form under physical conditions that are not greatly different from those found in the zones of surface alteration and sulphide enrichment where ores are exposed to the action of surface agencies.

The deposits formed at moderate and shallow depths by cold solutions include a large number of important deposits of lead and zinc in the Mississippi Valley and many copper deposits in Colorado, New Mexico, and Utah. Examples could be multiplied, but these define the type. The conditions under which these deposits form are doubtless closely similar to those which exist in zones of sulphide enrichment, and many of the minerals formed are found also in the secondary sulphide zones. Much evidence has been cited to show that these deposits were formed by ground water that gathered its metallic contents from great masses of rocks in which the metals were spar-

ingly disseminated. The metallic salts, chiefly sulphates and chlorides, were gathered in water channels, and the metals were deposited as sulphides where conditions were favorable. In many examples some form of organic material supplied the precipitating agent. If deposition had taken place on an older sulphide these deposits would be classed as secondary sulphide ores, but in general there is no evidence that bodies of older sulphide ore occupied the place of the deposits. These ores are therefore considered primary, although they have been leached by ground water from an older metalliferous rock.

ACKNOWLEDGMENTS.

During the 15 years that have passed since the first general papers on sulphide enrichment were issued a number of detailed reports have appeared, treating the geology and ore deposits of certain mining districts. In several of these papers the chemical processes involved are discussed in the light of the field relations of the deposits. The contributions of Lindgren, Ransome, Spencer, Boutwell, Irving, Graton, Spurr, Garrey, Ball, Butler, Lawson, Paige, Knopf, Umpleby, and Gordon are particularly valuable. Since 1905, when the work of collecting the mineral statistics of the United States was placed in the hands of field geologists, the annual reviews of resources, production, and development that have appeared in the reports entitled "Mineral resources of the United States" have been a never-failing source of information. The chapters on gold, by Waldemar Lindgren and H. D. McCaskey; those on copper, by L. C. Graton and B. S. Butler; those on lead and zinc, by C. E. Siebenthal; and those on the rare metals, by F. L. Hess, have furnished many valuable data.

Data on the chemistry of the processes of sulphide enrichment have been accumulated rapidly since 1900. The paper by Schuermann[1] published in 1888 was for many years the most important source of information respecting the behavior of sulphides in certain reactions involving double decomposition. In 1907 Weigel[2] published a paper showing the solubilities in water of the metallic sulphides, which, as was pointed out by R. C. Wells,[3] correspond closely in order to the series found by Schuermann. In 1903 H. V. Winchell[4] published the results of experiments in chalcocitization of sulphide ores. More recently experiments in the solution or precipitation of

[1] Schuermann, Ernst, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, p. 326, 1888.

[2] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, pp. 293–300, 1907.

[3] Wells, R. C., The fractional precipitation of sulphides: Econ. Geology, vol. 5, pp. 1–14, 1910.

[4] Winchell, H. V., Synthesis of chalcocite and its genesis at Butte, Mont.: Geol. Soc. America Bull., vol. 14, pp. 269–276, 1903.

the metals have been made by Sullivan, Wells, Allen, Stokes, Buehler and Gottschalk, Brokaw, Cooke, Grout, A. N. Winchell, and many others.

Since August, 1912, when an earlier bulletin[1] was transmitted for publication, many important papers have been published. Among them may be mentioned those on copper by Graton and Murdoch, Spencer, Ransome, Butler, Rogers, Ray, Tolman, and Clark; on silver by Cooke, Palmer and Bastin, Schrader, Grout, Nissen and Hoyt, and Ravicz; on gold by Brokaw, Lehner, Eddingfield, Umpleby, Paige, and Ferguson; on zinc by Siebenthal, Butler, Knopf, Loughlin, and Hill; on rare metals by Hess and Bancroft. These papers have served greatly to elucidate certain vexed problems of the genesis of ores of these metals. Several papers treating the general problem of superficial alteration are noteworthy. These include contributions of Lindgren, Krusch, Tolman, Grout, Nishihara, Wells, Hodge, and many others.

I wish to acknowledge my indebtedness to my colleagues of the United States Geological Survey, especially to Messrs. Waldemar Lindgren, F. L. Ransome, A. C. Spencer, F. L. Hess, Adolph Knopf, and B. S. Butler, who have read portions of this paper and have generously contributed unpublished data on certain districts. Dr. W. H. Hunter, of the University of Minnesota, and Mr. R. C. Wells, of the United States Geological Survey, have read critically certain parts of this paper, where the problems of physical chemistry are treated, and many of the reactions have been discussed with Dr. E. T. Allen and associates, of the Carnegie Geophysical Laboratory at Washington, and with Mr. F. W. Clarke, of the United States Geological Survey.

BIBLIOGRAPHY.

Most of the publications listed below discuss superficial alteration. The list includes particularly papers that illustrate the principles of alteration or describe regions where the process has occurred. A few references to papers treating underground waters and other subjects nearly related to enrichment are also listed. Many references to papers not listed below are made in this bulletin, particularly in the sections on mining districts.

ADAMS, F. D., An experimental contribution to the question of the depth of the zone of flow in the earth's crust: Jour. Geology, vol. 20, pp. 97–118, 1912.

ADAMS, G. I., Zinc and lead deposits of northern Arkansas: U. S. Geol. Survey Prof. Paper 24, pp. 39–46, 1904.

ALLEN, E. T., Sulphides of iron and their genesis: Min. and Sci. Press, vol. 103, pp. 413–414, 1911.

[1] Emmons, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, 1913.

ALLEN, E. T., CRENSHAW, J. L., and JOHNSTON, JOHN, The mineral sulphides of iron, with crystallographic study by E. S. Larsen: Am. Jour. Sci., 4th ser., vol. 33, p. 169, 1912; also Carnegie Inst. Washington Yearbook 9, p. 104, 1911.

ALLEN, E. T., and CRENSHAW, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 34, pp. 341–396, 1912.

ARGALL, PHILIP, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, pp. 282–288, 1914.

BAIN, H. F., Zinc and lead deposits of the upper Mississippi Valley: U. S. Geol. Survey Bull. 294, pp. 46–70, 1906.

BAIN, H. F., and VAN HISE, C. R., Preliminary report on the lead and zinc deposits of the Ozark region: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 23–227 (esp. pp. 95–162), 1901.

BALL, S. H., Copper deposits of the Hartville uplift, Wyoming: U. S. Geol. Survey Bull. 315, pp. 93–107, 1907.

BALL, S. H. See also Spurr, J. E., Garrey, G. H., and Ball, S. H.

BANCROFT, G. T., The formation and enrichment of ore-bearing veins: Am. Inst. Min. Eng. Trans., vol. 38, pp. 245–268, 1907.

BANCROFT, HOWLAND, Reconnaissance of the ore deposits in northern Yuma County, Ariz.: U. S. Geol. Survey Bull. 451, 130 pp., 1911.

BANCROFT, HOWLAND. See also Irving, J. D., and Bancroft, Howland.

BARD, D. C., Absence of secondary copper sulphide enrichment in calcite gangues: Econ. Geology, vol. 5, pp. 59–61, 1910.

BASTIN, E. S., Geology of the pitchblende ores of Colorado: U. S. Geol. Survey Prof. Paper 90, pp. 1–5 (Prof. Paper 90–A), 1914.

BASTIN, E. S., Metasomatism in downward sulphide enrichment: Econ. Geology, vol. 8, pp. 51–63, 1913.

BASTIN, E. S. See also Palmer, Chase, and Bastin, E. S.

BATEMAN, A. M. See Ferguson, H. G., and Bateman, A. M.

BAYLEY, W. S., The Menominee iron-bearing district of Michigan: U. S. Geol. Survey Mon. 46, 573 pp., 1904.

BECK, R., The nature of ore deposits, translated and revised by W. H. Weed, pp. 361–382, New York, 1905.

BECKER, G. F., Geology of the Comstock lode and the Washoe district: U. S. Geol. Survey Mon. 3, p. 273, 1882.

BECKER, G. F., Quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, xix, 486 pp., 1888.

BERGEAT, ALFRED, and STELZNER, A. W., Die Erzlagerstätten, Leipzig, 1906.

BLAKE, W. P., The caliche of southern Arizona; an example of deposition by the vadose circulation: Am. Inst. Min. Eng. Trans., vol. 31, pp. 220–226, 1901.

BLOW, A. A., The ore chutes and recent development of Iron Hill, Leadville, Colo.: Am. Inst. Min. Eng. Trans., vol. 18, pp. 145–181, 1890.

BOEHMER, MAX, Secondary enrichment and impoverishment: Econ. Geology, vol. 3, pp. 337–340, 1908.

BOUTWELL, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, 413 pp., 1905.

BOUTWELL, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, 231 pp., 1912.

BROCK, R. W., Preliminary report on the Boundary Creek district, British Columbia: Canada Geol. Survey Summary Rept. for 1902–3, pp. 90–136, 1903.

BROCK, R. W., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, pp. 204–205, 1911.

BROKAW, A. D., The solution of gold in the superficial alteration of ore bodies: Jour. Geology, vol. 18, pp. 320–326, 1910.

BROKAW, A. D., The secondary precipitation of gold in ore bodies: Jour. Geology, vol. 21, pp. 251–268, 1913.

BUCKLEY, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties, Mo.: Missouri Bur. Geology and Mines, vol. 9, pt. 1, 259 pp., 1909.

BUEHLER, H. A., and GOTTSCHALK, V. H., Oxidation of sulphides: Econ. Geology, vol. 5, pp. 28–35, 1910; vol. 7, pp. 15–35, 1912.

BUEHLER, H. A. See also Gottschalk, V. H., and Buehler, H. A.

BURCHARD, E. F., The Clinton iron ore deposits of Alabama: Am. Inst. Min. Eng. Trans., vol. 40, pp. 75–133, 1909.

BURCHARD, E. F., BUTTS, CHARLES, and ECKEL, E. C., Iron ores, fuels, and fluxes of the Birmingham district, Alabama: U. S. Geol. Survey Bull. 400, 204 pp., 1910.

BURGESS, J. A., The halogen salts of silver and associated minerals at Tonopah, Nev.: Econ. Geology, vol. 6, pp. 13–21, 1911.

BUTLER, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, 212 pp., 1913.

BUTLER, B. S., and GALE, H. S., Alunite; a newly discovered deposit near Marysvale, Utah: U. S. Geol. Survey Bull. 511, 64 pp., 1912.

BUTLER, B. S., and MCCASKEY, H. D., Copper ores of the New London mine [Frederick County, Md.]: Am. Inst. Min. Trans., vol. 49, pp. 284–291, 1915.

BUTLER, G. M., Some recent developments at Leadville: Econ. Geology, vol. 7, pp. 315–323, 1912, and vol. 8, pp. 1–18, 1913.

BUTTS, CHARLES. See Burchard, E. F., Butts, Charles, and Eckel, E. C.

CATHERINET, JULES, Copper Mountain, British Columbia: Eng. and Min. Jour., vol. 79, p. 125, 1905.

CHAMBERLIN, R. T., The gases in rocks: Jour. Geology, vol. 17, pp. 534–568, 1909.

CHANCE, H. M., A new theory of the genesis of brown hematite ore and the new source of sulphur supply: Am. Inst. Min. Eng. Trans., vol. 39, pp. 522–539, 1908.

CHURCH, J. A., The Tombstone, Ariz., mining district: Am. Inst. Min. Eng. Trans., vol. 33, pp. 3–37, 1902.

CHURCH, J. A., The Comstock lode, its formation and history, New York, 1879.

CLARK, ELLIS, The silver mines of Lake Valley, N. Mex.: Am. Inst. Min. Eng. Trans., vol. 24, pp. 138–167, 1895.

CLARKE, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, 821 pp., 1916.

CLARK, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull. 75, pp. 77–150, 1914.

CLARK, J. D. See also Tolman, C. F., jr., and Clark, J. D.

COOKE, H. C., The secondary enrichment of silver ores: Jour. Geology, vol. 21, pp. 1–29, 1913.

CORNU, F., Die Bedeutung gelartiger Körper in der Oxydationszone der Erzlagerstätten: Zeitschr. prakt. Geologie, vol. 17, pp. 81–87, 1909.

CRANE, W. R. See Haworth, Erasmus, Crane, W. R., and Rogers, A. F.

CRAWFORD, R. D., A preliminary report on the geology of the Monarch mining district, Colo.: Colorado Geol. Survey Bull. 1, 78 pp., 1910.

CROSS, WHITMAN, and PENROSE, R. A. F., Jr., Geology and mining industries of the Cripple Creek district, Colorado: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, pp. 1–209, 1895.

DE LAUNAY, L., Formation des gîtes métallifères, 2d ed., Paris, 1893.

DE LAUNAY, L. See also Fuchs, E., and De Launay, L.

DICKSON, C. W., The ore deposits of Sudbury, Canada: Am. Inst. Min. Eng. Trans., vol. 34, pp. 3–67, 1903.

DICKSON, C. W., The distribution of platinum metals in other sources than placers: Canadian Min. Inst. Jour., vol. 8, pp. 192–214, 1905.

DILLER, J. S., The Bohemia mining region of western Oregon: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, pp. 7–64, 1900.

DOELTER, C., Handbuch der Mineralchemie, Bd. 1, Vienna, 1912.

DOUGLAS, JAMES, The Copper Queen mine, Arizona: Am. Inst. Min. Eng. Trans., vol. 29, pp. 511–545, 1910.

ECKEL, E. C. See Burchard, E. F., Butts, Charles, and Eckel, E. C.

EDDINGFIELD, F. T., Alteration and enrichment in calcite-quartz-manganese gold deposits in the Philippine Islands: Philippine Jour. Sci., vol. 8, No. 2, Sec. A, pp. 125–134, April, 1913.

ELSING, M. T., Relations of outcrops to ore at Cananea: Eng. and Min. Jour., vol. 95, pp. 357–362, 1913.

EMMENS, S. H., The chemistry of gossan: Eng. and Min. Jour., vol. 54, pp. 582–583, 1892.

EMMONS, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, xxix, 770 pp., 1886.

EMMONS, S. F., The secondary enrichment of ore deposits: Am. Inst. Min. Eng. Trans., vol. 30, pp. 177–217, 1901.

EMMONS, S. F. See also Weed, W. H., Emmons, S. F., and Tower, G. W.

EMMONS, W. H., A genetic classification of minerals: Econ. Geology, vol. 3, pp. 611–627, 1908.

EMMONS, W. H., Outcrops of ore bodies: Min. and Sci. Press, vol. 99, pp. 751–759, 782–787, 1909.

EMMONS, W. H., The Cashin mine, Montrose County, Colo.: U. S. Geol. Survey Bull. 285, pp. 125–128, 1906.

EMMONS, W. H., The composition of the primary ore as a factor determining the vertical extent of the secondary sulphide zone: Cong. géol. internat., 12th sess., Toronto, Canada, Compt. rend., pp. 1–15, 1913.

EMMONS, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, pp. 3–73, 1912; Jour. Geology, vol. 19, pp. 15–46, 1911.

EMMONS, W. H., The enrichment of sulphide ores: U. S. Geol. Survey Bull. 529, 260 pp., 1912.

EMMONS, W. H., and CALKINS, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, 272 pp., 1912.

EMMONS, W. H., and HARRINGTON, G. L., A comparison of the waters of mines and hot springs: Econ. Geology, vol. 8, pp. 653–669, 1913.

EMMONS, W. H., and LANEY, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.: U. S. Geol. Survey Bull. 470, pp. 151–172, 1911.

EMMONS, W. H., and LARSEN, E. S., A preliminary report on the geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. 530, pp. 42–65, 1913.

EULER, HANS, Ueber Löslichkeitserniedrigung: Zeitschr. physikal. Chemie, vol. 49, p. 314, 1904.

FARREL, J. H., Practical field geology, New York, 1912.

FERGUSON, H. G., Gold lodes of the Weaverville quadrangle, Colorado: U. S. Geol. Sur[illegible] Bull. 540, pp. 22–81, 1914.

FERGUSON, H[illegible] and BATEMAN, A. M., Geologic features of tin deposits: Econ. Geology, [illegible] 209–262, 1912.

FERNEKES, G., Precipitation of copper from chloride solutions by means of ferrous chloride: Econ. Geology, vol. 2, pp. 580–581, 1907.

FINCH, J. W., A geological journey in Guerrero: Min. and Sci. Press, vol. 101, p. 498, 1910.

FINCH, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, pp. 193–252, 1904.

FINLAYSON, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, pp. 410–420, 1910.

FREE, E. E., The solubility of precipitated basic copper carbonate in solutions of carbon dioxide: Am. Chem. Soc. Jour., vol. 30, pp. 1366–1374, 1908.

FUCHS, E., and DE LAUNAY, L., Traité des gîtes minéraux et métallifères, 1893.

GALE, H. S., Carnotite in western Colorado: U. S. Geol. Survey Bull. 340, pp. 256–262, 1908.

GALE, H. S. See also Butler, B. S., and Gale, H. S.

GEORGE, R. D., The main tungsten area of Boulder County, Colo.: Colorado Geol. Survey Ann. Rept. for 1908, pp. 7–103, 1909.

GILBERT, C. G., and POGUE, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., vol. 45, pp. 609–625, 1913.

GOLDSCHMIDT, V. M., Die Kontaktmetamorphose im Kristianiagebiet, 1911.

GORDON, C. H. See Lindgren, Waldemar, Graton, L. C., and Gordon, C. H.

GOTTSCHALK, V. H., and BUEHLER, H. A., Oxidation of sulphides: Econ. Geology, vol. 7, pp. 15–34, 1912.

GOTTSCHALK, V. H. See also Buehler, H. A., and Gottschalk, V. H.

GRANT, U. S., Report on lead and zinc deposits of Wisconsin: Wisconsin Geol. and Nat. Hist. Survey Bull. 14, 100 pp., 1906.

GRATON, L. C., Reconnaissance of some gold and tin deposits of the southern Appalachians, with notes on the Dahlonega mines by Waldemar Lindgren: U. S. Geol. Survey Bull. 293, 134 pp., 1906.

GRATON, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, pp. 71–111, 1910.

GRATON, L. C., and MURDOCH, JOSEPH, The sulphide ores of copper; some results of micrographic study: Am. Inst. Min. Eng. Trans., vol. 45, pp. 26–82, 1914.

GRATON, L. C. See also Lindgren, Waldemar, Graton, L. C., and Gordon, C. H.

GREGORY, J. W., Factors that control the depths of ore deposits: Australian Inst. Min. Eng. Trans., vol. 8, pp. 127–154, 1904.

GROUT, F. F., The oxidation of pyrite: Econ. Geology, vol. 3, pp. 532–534, 1908.

GROUT, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, pp. 407–433, 1913.

GUNTHER, C. C., Examination of prospects, New York, 1912.

HARDER, E. C., Manganese deposits of the United States, with sections on foreign deposits, chemistry, and uses: U. S. Geol. Survey Bull. 427, 208 pp., 1910.

HARDER, E. C., Some chromite deposits of western and central California: U. S. Geol. Survey Bull. 430, pp. 167–183, 1910.

HARDER, E. C., The iron ores of the Appalachian region in Virginia: U. S. Geol. Survey Bull. 380, pp. 188–198, 1909.

HASTINGS, J. B., Association of magnetite with sulphides in mineral deposits: Min. and Sci. Press, vol. 97, pp. 332–338, 358–359, 1908.

HAWORTH, ERASMUS, CRANE, W. R., and ROGERS, A. F., Special report on lead and zinc: Kansas Geol. Survey, vol. 8, xv, 543 pp., 1904.

HAYES, C. W., Geological relations of iron ores in the Cartersville district, Georgia: Am. Inst. Min. Eng. Trans., vol. 30, pp. 403–419, 1900.

HAYES, C. W., The Arkansas bauxite deposits: U. S. Geol. Survey Twenty-first Ann. Rept., pt. 3, pp. 435–472, 1901.

HERSHEY, O. H., Genesis of the lead-silver ores in Wardner district, Idaho: Min. and Sci. Press, vol. 104, pp. 750–753, 786–790, 825–827, 1912.

HERSHEY, O. H., Primary chalcocite in California: Min. and Sci. Press, vol. 96, p. 429, 1908.

HERSHEY, O. H., Geology at Treadwell mines, in Bain, H. F., and others, Types of ore deposits, pp. 157–171, San Francisco, 1911.

HESS, F. L., A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, vol. 9, pp. 675–688, 1914.

HESS, F. L., Notes on vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, pp. 142–160, 1913.

HESS, F. L., The Arkansas antimony deposits: U. S. Geol. Survey Bull. 340, pp. 241–252, 1908.

HESS, F. L., The arsenopyrite deposits of Brinton, Va.: U. S. Geol. Survey Bull. 470, pp. 205–211, 1912.

HESS, F. L., Some molybdenum deposits of Maine, Utah, and California: U. S. Geol. Survey Bull. 340, pp. 231–240, 1908.

HESS, F. L., Vanadium in the Sierra de los Caballos, N. Mex.: U. S. Geol. Survey Bull. 530, pp. 157–160, 1913.

HESS, F. L., and GRATON, L. C., The occurrence and distribution of tin: U. S. Geol. Survey Bull. 260, pp. 161–187, 1905.

HESS, F. L., and SCHALLER, W. T., Colorado ferberite and the wolframite series: U. S. Geol. Survey Bull. 583, 75 pp., 1914.

HEWETT, D. F., The occurrence of vanadium in Peru: Am. Inst. Min. Eng. Trans., vol. 40, pp. 274–299, 1909.

HILL, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, pp. 223–275, 1914.

HILL, J. M. See Schrader, F. C., and Hill, J. M.

HODGE, E. T., Composition of waters in mines of sulphide ores: Econ. Geology, vol. 10, pp. 123–140, 1915.

HOOVER, H. C., The superficial alteration of western Australian ore deposits: Am. Inst. Min. Eng. Trans., vol. 28, pp. 758–765, 1888.

HORE, R. E., Origin of cobalt-silver ores of northern Ontario: Econ. Geology, vol. 3, pp. 599–610, 1908.

HUNTER, J. F., Some cerusite deposits in Custer County, Colo.: U. S. Geol. Survey Bull. 580 (Bull. 580–C), p. 34, 1914.

HYNES, D. P., Notes on the geology of the Mina Mexico vein: Econ. Geology, vol. 7, pp. 280–286, 1912.

IRVING, J. D., Some features of replacement ore bodies and the criteria by which they may be recognized: Econ. Geology, vol. 6, pp. 527–561, 1911; also in Bain, H. F., and others, Types of ore deposits, pp. 220–298, San Francisco, 1911.

IRVING, J. D., Economic resources of the northern Black Hills: U. S. Geol. Survey Prof. Paper 26, 222 pp., 1904.

IRVING, J. D., and BANCROFT, HOWLAND, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, 128 pp., 1911.

JACKSON, D. D., The normal distribution of chlorine in the natural waters of New York and New England: U. S. Geol. Survey Water-Supply Paper 144, 31 pp., 1905.

JORALEMON, I. B., The Ajo copper mining district: Am. Inst. Min. Eng. Trans., vol. 49, pp. 593–609, 1915.

KEMP, J. F., Secondary enrichment of ore deposits of copper: Econ. Geology, vol. 1, pp. 11–25, 1906.

KEMP, J. F., The rôle of igneous rocks in the formation of veins, in Pošepný, Franz, The genesis of ore deposits, pp. 169–198, 1901.

KEMP, J. F., Waters, meteoric and magmatic: Min. and Sci. Press, vol. 96, pp. 705, 709, 1908.

KEYES, C. R., Cerargyrite ores, their genesis and geology: Econ. Geology, vol. 2, pp. 774–780, 1907.

KEYES, C. R., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, pp. 558–564, 1910.

KEYES, C. R., Origin of certain bonanza silver ores of the arid regions: Am. Inst. Min. Eng. Trans., vol. 42, pp. 500–517, 1911.

KEYES, C. R., Porphyry coppers: Min. and Met. Soc. America Bull. 25, pp. 316–320, 1910.

KING, F. H., Principles and conditions of the movement of ground water: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, pp. 67–294, 1898.

KING, L. V., On the limiting strength of rocks under conditions of stress existing in the earth's interior: Jour. Geology, vol. 20, pp. 119–139, 1912.

KIRK, C. T., Conditions of mineralization in the copper veins at Butte, Mont.: Econ. Geology, vol. 7, pp. 35–82, 1912.

KNOPF, ADOLPH, Notes on the foothill copper belt of the Sierra Nevada: California Univ. Dept. Geology Bull., vol. 4, No. 17, pp. 411–423, 1906.

KNOPF, ADOLPH, Ore deposits of the Helena mining region, Montana: U. S. Geol. Survey Bull. 527, 143 pp., 1912.

KNOPF, ADOLPH, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, pp. 81–120, 1914.

KNOPF, ADOLPH, Some features of Alaska tin deposits: Econ. Geology, vol. 4, pp. 214–223, 1909.

KRUSCH, P., Primäre und sekundäre Erze unter besonderer Berücksichtigung der "gel" und der "schwermetallreichen" Erze: Cong. géol. internat., 12th session, Toronto, Canada, Compt. rend., pp. 275–286, 1914.

LANE, A. C., Mine waters: Lake Superior Min. Inst. Proc., vol. 13, pp. 63–152, 1908.

LANE, A. C., Michigan iron mines and their mine waters: Canadian Min. Inst. Jour., vol. 12, pp. 114–129, 1909.

LANE, A. C., Mine water composition an index to the course of ore-bearing currents: Econ. Geology, vol. 9, pp. 239–263, 1914.

LANE, A. C., Native copper deposits, in Bain, H. F., and others, Types of ore deposits, pp. 133–139, San Francisco, 1911.

LANEY, F. B., The relation of bornite and chalcocite in the copper ores of the Virgilina district of North Carolina and Virginia: Econ. Geology, vol. 6, pp. 399–411, 1911.

LANEY, F. B. See also Emmons, W. H., and Laney, F. B.

LARSEN, E. S. See Emmons, W. H., and Larsen, E. S.; Wright, F. E., and Larsen, E. S.

LAWSON, A. C., The copper deposits of the Robinson district, Nevada: California Univ. Dept. Geol. Bull., vol. 4, pp. 287–357, 1906.

LAZAREVIC, M., Die Enargit-Covellin-Lagerstätte von Cuka-Dulkan bei Bor in Ost-Serbien: Zeitschr. prakt. Geologie, vol. 20, pp. 337–369, 1912.

LEHNER, V. C., Some observations on the tellurides: Econ. Geology, vol. 4, pp. 544–564, 1909.

LEHNER, V. C., Transportation and deposition of gold in nature: Econ. Geology, vol. 9, pp. 523–528, 1914.

LEITH, C. K., Genesis of Lake Superior iron ores: Econ. Geology, vol. 1, pp. 47–65, 1905.

LEITH, C. K., Geology of the Cuyuna iron range, Minn.: Econ. Geology, vol. 2, pp. 145–152, 1907.

LEITH, C. K., Lake Superior type of iron-ore deposits, in Bain, H. F., and others, Types of ore deposits, pp. 53–76, San Francisco, 1911.

LEITH, C. K., The Mesabi iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 3, 316 pp., 1903.

LEITH, C. K., and HARDER, E. C., The iron ores of Iron Springs district, southern Utah: U. S. Geol. Survey Bull. 338, 102 pp., 1908.

LEITH, C. K. See also Van Hise, C. R., and Leith, C. K.

LEWIS, J. V., Copper deposits of the New Jersey Triassic: Econ. Geology, vol. 2, pp. 242–257, 1907.

LINDGREN, WALDEMAR, Anhydrite as a gangue mineral: Econ. Geology, vol. 5, pp. 521–527, 1910.

LINDGREN, WALDEMAR, Metallogenetic epochs: Econ. Geology, vol. 4, pp. 409–420, 1909; also in Canadian Min. Inst. Jour., vol. 12, pp. 102–113, 1909.

LINDGREN, WALDEMAR, Mineral deposits, pp. 773–844, New York, 1913.

LINDGREN, WALDEMAR, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, 375 pp., 1905.

LINDGREN, WALDEMAR, The relations of ore deposition to physical conditions: Econ. Geology, vol. 2, pp. 105–127, 1907.

LINDGREN, WALDEMAR, GRATON, L. C., and GORDON, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, 361 pp., 1910.

LINDGREN, WALDEMAR, and RANSOME, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, 516 pp., 1906.

LOUGHLIN, G. F., The oxidized zinc ores of the Tintic district, Utah: Econ. Geology, vol. 9, pp. 1–12, 1914.

MCCASKEY, H. D., Notes on some gold deposits of Alabama: U. S. Geol. Survey Bull. 340, pp. 36–52, 1908.

MCCASKEY, H. D., Precious and semiprecious metals in the Eastern States in 1912: U. S. Geol. Survey Mineral Resources, 1912, pt. 1, pp. 417–436, 1913.

MCCASKEY, H. D., Quicksilver: U. S. Geol. Survey Mineral Resources, 1911, pt. 1, pp. 889–921, 1912.

MCCASKEY, H. D. See also Butler, B. S., and McCaskey, H. D.

MCCAUGHEY, W. J., The solvent effect of ferric and cupric solutions upon gold: Am. Chem. Soc. Jour., vol. 31, pp. 1261–1270, 1909.

MADDREN, A. G. See Moffit, F. H., and Maddren, A. G.

MILLER, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, 279 pp., 1913.

MOFFIT, F. H., and MADDREN, A. G., Mineral resources of the Kotsina-Chitina region, Alaska: U. S. Geol. Survey Bull. 374, pp. 80–86, 1909.

MURDOCH, JOSEPH. See Graton, L. C., and Murdoch, Joseph.

NISHIHARA, G. S., The rate of reduction of acidity of descehding waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, pp. 743–757, 1914.

PAIGE, SIDNEY, Mineral resources of the Llano-Burnet region, Texas, with an account of the pre-Cambrian geology: U. S. Geol. Survey Bull. 450, pp. 56–69, 1911.

PAIGE, SIDNEY, Metalliferous ore deposits near the Burro Mountains, Grant County, N. Mex.: U. S. Geol. Survey Bull. 470, pp. 131–150, 1911.

PAIGE, SIDNEY, The origin of turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 7, pp. 382–392, 1912.

PALMER, CHASE, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 31 pp., 1911.

PALMER, CHASE, Studies in silver enrichment; tetranickel-triarsenide, its capacity as a silver precipitant: Econ. Geology, vol. 9, pp. 664–674, 1914.

PALMER, CHASE, and BASTIN, E. S., Metallic minerals as precipitants of gold and silver: Econ. Geology, vol. 8, pp. 140–171, 1913.

PEARCE, RICHARD, Discussion of paper by T. A. Rickard on The origin of the gold-bearing quartz of the Bendigo Reefs, Australia: Am. Inst. Min. Eng. Trans., vol. 22, pp. 738–774, 1894.

PEARCE, RICHARD, Further notes on Cripple Creek ores: Colorado Sci. Soc. Proc., vol. 5, pp. 11–16, 1896.

PENROSE, R. A. F., Jr., Certain phases of superficial diffusion in ore deposits: Econ. Geology, vol. 9, pp. 20–24, 1914.

PENROSE, R. A. F., Jr., Manganese, its uses, ores, and deposits: Arkansas Geol. Survey Ann. Rept. for 1890, vol. 1, 642 pp., 1891.

PENROSE, R. A. F., Jr., Some causes of ore shoots: Econ. Geology, vol. 5, pp. 97–132, 1910; also in Bain, H. F., and others, Types of ore deposits, pp. 324–353, San Francisco, 1911.

PENROSE, R. A. F., Jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, pp. 288–317, 1892.

PENROSE, R. A. F., Jr., See also Cross, Whitman, and Penrose, R. A. F., jr.

PRATT, J. H., The occurrence, origin, and chemical composition of chromite: Am. Inst. Min. Eng. Trans., vol. 29, pp. 17–39, 1899.

PURINGTON, C. W., Preliminary report on the mining industries of the Telluride quadrangle, Colorado: U. S. Geol. Survey Eighteenth Ann. Rept., pt. 3, pp. 838–841, 1908.

RANSOME, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: U. S. Geol. Survey Bull. 182, 265 pp., 1901.

RANSOME, F. L., Copper deposits near Superior, Ariz.: U. S. Geol. Survey Bull. 540, pp. 139–159, 1914.

RANSOME, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, pp. 202–220, 1910.

RANSOME, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, 168 pp., 1903; also in U. S. Geol. Survey Bull. 529, pp. 183–186, 1913.

RANSOME, F. L., Geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, 258 pp., 1909.

RANSOME, F. L., Jerome, Ariz., in U. S. Geol. Survey Bull. 529, pp. 192–193, 1913.

RANSOME, F. L., Ray, Ariz., in U. S. Geol. Survey Bull. 529, pp. 186–187, 1913.

RANSOME, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, 168 pp., 1904; also in U. S. Geol. Survey Bull. 529, pp. 179–182, 1913.

RANSOME, F. L., and CALKINS, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, 203 pp., 1908.

RANSOME, F. L. See also Lindgren, Waldemar, and Ransome, F. L.

RAVICZ, L. G., Experiments in the enrichment of silver ores: Econ. Geology, vol. 10, pp. 368–392, 1915.

RAY, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, pp. 463–481, 1914.

READ, T. T., The secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 37, pp. 297–303, 1906.

REID, J. A., The structure and genesis of the Comstock lode: California Univ. Dept. Geology Bull., vol. 4, pp. 189–192, 1906.

RICHARDSON, G. B., Antimony in southern Utah: U. S. Geol. Survey Bull. 340, pp. 253–256, 1908.

RICKARD, FORBES, Notes on tungsten deposits of Arizona: Eng. and Min. Jour., vol. 78, pp. 263–265, 1904.

RICKARD, T. A., The Bendigo gold field: Am. Inst. Min. Eng. Trans., vol. 20, pp. 462–545, 1891.

RICKARD, T. A., The Cripple Creek volcano: Am. Inst. Min. Eng. Trans., vol. 30, pp. 367–403, 1900.

RICKARD, T. A., The Enterprise mine, Rico, Colo.: Am. Inst. Min. Eng. Trans., vol. 26, pp. 906–980, 1896.

RICKARD, T. A., The formations of bonanzas in the upper portions of gold veins: Am. Inst. Min. Eng. Trans., vol. 31, pp. 198–220, 1901; also in Pošepný, Franz, The genesis of ore deposits, pp. 734–755, 1902.

RICKARD, T. A., The persistence of ore in depth: Min. and Sci. Press, vol. 105, pp. 232–236, 1912.

RICKARD, T. A., Water in mines, a theory: Eng. and Min. Jour., vol. 75, pp. 402–403, 589–590, 1903.

RICKARD, T. A., Waters, meteoric and magmatic: Min. and Sci. Press, vol. 96, pp. 872–875, 1908.

RICKETTS, L. D., The ores of Leadville and their modes of occurrence, p. 37, Princeton, N. J., 1883.

ROGERS, A. F., A new synthesis and new occurrences of covellite: Columbia Univ. School of Mines Quart., vol. 32, pp. 298–304, 1911.

ROGERS, A. F., Minerals observed on buried Chinese coins of the seventh century: Am. Geologist, vol. 31, pp. 43–46, 1903.

ROGERS, A. F., Notes on some pseudomorphs, petrefactions, and alterations: Am. Philos. Soc. Proc., vol. 49, pp. 17–22, 1910.

ROGERS, A. F., Upward secondary sulphide enrichment and chalcocite formation at Butte, Mont.: Econ. Geology, vol. 8, pp. 781–795, 1913.

ROGERS, A. F. See also Haworth, Erasmus, Crane, W. R., and Rogers, A. F.

SALES, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, pp. 681–682, 1910.

SALES, R. H., Ore shoots at Butte, Mont.: Econ. Geology, vol. 3, pp. 326–331, 1908.

SALES, R. H., Superficial alteration of the Butte veins: Econ. Geology, vol. 5, pp. 15–21, 1910.

SALES, R. H., Ore deposits at Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 46, pp. 3–106, 1913.

SANFORD, SAMUEL, and STONE, R. W., Useful minerals of the United States: U. S. Geol. Survey Bull. 585, 250 pp., 1914.

SCHALLER, W. T. See Hess, F. L., and Schaller, W. T.

SCHRADER, F. C., A reconnaissance of the Jarbridge, Contact, and Elk Mountain mining districts, Elko County, Nev.: U. S. Geol. Survey Bull. 497, 162 pp., 1912.

SCHRADER, F. C., and HILL, J. M., Some occurrences of molybdenite in the Santa Rita and Patagonia Mountains, Ariz.: U. S. Geol. Survey Bull. 430, pp. 154–163, 1910.

SCHUERMANN, ERNST, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, p. 326, 1888.

SEGALL, JULIUS, The origin and occurrence of certain crystallographic intergrowths: Econ. Geology, vol. 10, pp. 462–470, 1915.

SEIDELL, ATHERTON, Solubilities of inorganic and organic substances, New York, 1911.

SHARWOOD, W. J., Analyses of some rocks and minerals from the Homestake mine, Lead, S. Dak.: Econ. Geology, vol. 6, pp. 729–789, 1911.

SIEBENTHAL, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), 1907 (reprinted, 1914).

SIEBENTHAL, C. E., Cadmium: U. S. Geol. Survey Mineral Resources, 1908, pt. 1, pp. 794–803, 1909.

SIEBENTHAL, C. E., Origin of the zinc and lead deposits of the Joplin region, Missouri, Kansas, and Oklahoma: U. S. Geol. Survey Bull. 606, 283 pp., 1915.

SIEBENTHAL, C. E., Spring deposits at Sulphur Springs, Ark., with microscopic examination by H. E. Merwin: Econ. Geology, vol. 9, pp. 758–767, 1914.

SIMPSON, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, pp. 628–636, 1908.

SINGEWALD, J. T., Jr., The Erzgebirge tin deposits: Econ. Geology, vol. 5, pp. 160–177, 265–272, 1910.

SINGEWALD, J. T., Jr., The Mount Roudny gold deposit: Econ. Geology, vol. 5, pp. 257–264, 1910.

SLICHTER, C. S., Theoretical investigation of the motion of ground waters: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, pp. 295–384, 1899.

SLICHTER, C. S., The motions of underground waters: U. S. Geol. Survey Water-Supply Paper 67, 106 pp., 1902.

SMITH, G. O. See Tower, G. W., and Smith, G. O.; Tower, G. W., Smith, G. O., and Emmons, S. F.

SMITH, GEORGE, The ore deposits of the Australian Broken Hill Consols mine, Broken Hill, New South Wales: Am. Inst. Min. Eng. Trans., vol. 26, pp. 69–78, 1897.

SMYTH, C. H., Jr., On the Clinton iron ores: Am. Jour. Sci., 3d ser., vol. 43, pp. 487–496, 1892.

SMYTH, C. H., Jr., The Clinton type of iron-ore deposits, in Bain, H. F., and others, Types of ore deposits, pp. 33–52, San Francisco, 1911.

SOMMERLAD, HERMANN, Über einige Versuche zur Herstellung von Sulfantimoniten und Sulfarseniten des Silbers auf trockenem Wege: Zeitschr. anorg. Chemie, vol. 15, pp. 173–179, 1897; Über Versuche zur Darstellung von Sulfantimoniten und Sulfarseniten des Silbers, Kupfers, und Bleis auf trockenem Wege: Idem, vol. 18, pp. 420–447, 1898.

SPENCER, A. C., Chalcocite deposition: Econ. Geology, vol. 8, pp. 621–652, 1913.

SPENCER, A. C., The copper deposits of the Encampment district, Wyoming: U. S. Geol. Survey Prof. Paper 25, 107 pp., 1904.

SPENCER, A. C., The geology of the Treadwell ore deposits, Douglas Island, Alaska: Am. Inst. Min. Eng. Trans., vol. 35, pp. 473–511, 1904.

SPENCER, A. C., Three deposits of iron ore in Cuba: U. S. Geol. Survey Bull. 340, pp. 318–329, 1908.

SPURR, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, XXXV, 260 pp., 1898.

SPURR, J. E., The ore deposits of Monte Christo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 777–865, 1901.

SPURR, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, 295 pp., 1905.

SPURR, J. E., The iron-bearing rocks of the Mesabi range, in Minnesota: Minnesota Geol. and Nat. Hist. Survey Bull. 10, viii, 259 pp., 1894.

SPURR, J. E., Ore deposition at Aspen, Colo.: Econ. Geology, vol. 4, pp. 301–320, 1909.

SPURR, J. E., and GARREY, G. H., Ore deposits of the Velardeña district, Mexico: Econ. Geology, vol. 3, pp. 688–725, 1908.

SPURR, J. E., GARREY, G. H., and BALL, S. H., Economic geology of the Georgetown quadrangle (together with the Empire district), Colorado: U. S. Geol. Survey Prof. Paper 63, 422 pp., 1908.

STEIDTMANN, EDWARD, A graphic comparison of the alteration of rocks by weathering with their alteration by hot solutions: Econ. Geology, vol. 3, pp. 381–409, 1908.

STEWART, C. A. See Welsh, T. W. B., and Stewart, C. A.

STOKES, H. N., On the solution, transportation, and deposition of copper, silver, and gold: Econ. Geology, vol. 1, pp. 644–650, 1906.

STOKES, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, pp. 12–23, 1907.

STONE, R. W. See Sanford, Samuel, and Stone, R. W.

SULLIVAN, E. C., The interaction between minerals and water solutions, with special reference to geologic phenomena: U. S. Geol. Survey Bull. 312, pp. 37–64, 1907.

SULLIVAN, E. C., The secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 37, pp. 893–895, 1907.

TARR, W. A., Copper in the red beds of Oklahoma: Econ. Geology, vol. 5, pp. 221–226, 1910.

TOLMAN, C. F., Jr., Disseminated chalcocite deposits at Ray, Ariz.: Min. and Sci. Press, vol. 99, pp. 622–624, 1909.

TOLMAN, C. F., Jr., The Miami-Inspiration ore zone: Min. and Sci. Press, vol. 99, pp. 646–648, 1909.

TOLMAN, C. F., Jr., The southern Arizona copper fields: Min. and Sci. Press, vol. 99, pp. 356–369, 390–393, 1909.

TOLMAN, C. F., Jr., Secondary sulphide enrichment: Min. and Sci. Press, vol. 106, pp. 38–43, 141–145, 178–181, 1913.

TOLMAN, C. F., Jr., and CLARK, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions and the dispersion and precipitation of copper sulphides from colloidal suspensions, with a geological discussion: Econ. Geology, vol. 9, pp. 559–592, 1914.

TOWER, G. W., and SMITH, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, pp. 603–767, 1899.

TOWER, G. W., SMITH, G. O., and EMMONS, S. F., U. S. Geol. Survey Geol. Atlas, Tintic special folio (No. 65), 1909.

UMPLEBY, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, 182 pp., 1913.

UMPLEBY, J. B., Some ore deposits in northwestern Custer County, Idaho: U. S. Geol. Survey Bull. 539, 104 pp., 1913.

VAN HISE, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, 1286 pp., 1904.

VAN HISE, C. R., Principles of pre-Cambrian North American geology: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 1, pp. 571–874, 1896.

VAN HISE, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng. Trans., vol. 30, pp. 27–177, 1901.

VAN HISE, C. R., and LEITH, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, 641 pp., 1911.

VOGT, J. H. L., Das Huelva-Kiesfeld in Süd-Spanien und dem angrenzenden Theile von Portugal: Zeitschr. prakt. Geologie, vol. 7, pp. 241–254, July, 1899.

VOGT, J. H. L., Problems in the geology of ore deposits: Am. Inst. Min. Eng. Trans., vol. 31, pp. 125–169, 1901; also in Pošepný, Franz, The genesis of ore deposits, p. 675. 1902.

VOGT, J. H. L., Ueber die Bildung des gediegenen Silbers, besonders des Kongsberger Silbers, durch Secondärprocesse aus Silberglanz und anderen Silbererzen: Zeitschr. prakt. Geologie, vol. 7, pp. 113–123, 177–181, 1899.

WATSON, T. L., Geological relations of manganese ore deposits of Georgia: Am. Inst. Min. Eng. Trans., vol. 34, pp. 207–254, 1903.

WATSON, T. L., Lead and zinc deposits of the Virginia-Tennessee region: Am. Inst. Min. Eng. Trans., vol. 36, pp. 681–737, 1908.

WEED, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, 1912.

WEED, W. H., Geology of the Little Belt Mountains, Mont., with notes on the mineral deposits of the Neihart, Barker, Yogo, and other districts, accompanied by a report on the petrography of the igneous rocks of the district by L. V. Pirsson: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, pp. 257–581, 1900.

WEED, W. H., The enrichment of gold and silver veins: Am. Inst. Min. Eng. Trans., vol. 30, pp. 424–448, 1901; also in Pošepný, Franz, The genesis of ore deposits, 1902.

WEED, W. H., EMMONS, S. F., and TOWER, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), 1897.

WEIGEL, OSKAR, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, pp. 293–300, 1907.

WELLS, R. C., Electric activity in ore deposits: U. S. Geol. Survey Bull. 548, 78 pp., 1914.

WELLS, R. C., The fractional precipitation of sulphides: Econ. Geology, vol. 5, pp. 12–13, 1910.

WELLS, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, pp. 17–23, 1911.

WELLS, R. C., Fractional precipitation of some ore-forming compounds: U. S. Geol. Survey Bull. 609, 46 pp., 1915.

WELSH, T. W. B., and STEWART, C. A., Note on the effect of calcite gangue on the secondary enrichment of copper veins: Econ. Geology, vol. 7, pp. 785–787, 1912.

WENDT, A. F., The Potosi, Bolivia, silver district: Am. Inst. Min. Eng. Trans., vol. 19, pp. 74–107, 1891.

WHITMAN, A. R., The vadose synthesis of pyrite: Econ. Geology, vol. 8, pp. 455–468, 1913.

WHITNEY, J. D., Remarks on the changes which take place in the structure and composition of mineral veins near the surface, with particular reference to the East Tennessee copper mines: Am. Jour. Sci., 2d ser., vol. 20, pp. 53–57, 1855.

WINCHELL, A. N., Mining districts of the Dillon quadrangle, Montana, and adjacent areas: U. S. Geol. Survey Bull. 574, 191 pp., 1914.

WINCHELL, A. N., The oxidation of pyrite: Econ. Geology, vol. 2, pp. 290–294, 1907.

WINCHELL, H. V., Prospecting in the North: Min. Mag., vol. 3, pp. 436–438, 1910.

WINCHELL, H. V., Synthesis of chalcocite and its genesis at Butte, Mont.: Geol. Soc. America Bull., vol. 14, pp. 269–276, 1903; also in Eng. and Min. Jour., vol. 75, pp. 783–784, 1903.

WINCHELL, H. V., The Mesabi iron range: Minnesota Geol. and Nat. Hist. Survey Twentieth Ann. Rept., for 1891, pp. 111–180, 1893; Am. Inst. Min. Eng. Trans., vol. 21, pp. 644–686, 1892.

WINCHELL, N. H., The geology of Minnesota: Minnesota Geol. and Nat. Hist. Survey Final Rept., vol. 4, 630 pp., 1899.

WINSLOW, ARTHUR, The disseminated lead ores of southeastern Missouri: U. S. Geol. Survey Bull. 132, 31 pp., 1896.
WRIGHT, C. W., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, p. 359, 1911.
WRIGHT, F. E. and C. W., The Ketchikan and Wrangell mining districts, Alaska: U. S. Geol. Survey Bull. 347, 1908.
WRIGHT, F. E., and LARSEN, E. S., Quartz as a geologic thermometer: Am. Jour. Sci., 4th ser., vol. 27, p. 421, 1909.
WURTZ, HENRY, Contributions to analytical chemistry: Am. Jour. Sci., 2d ser., vol. 26, p. 51, 1858.

PHYSICAL CONDITIONS OF ENRICHMENT.

The processes of superficial alteration depend on the physical conditions, environment, and the geologic history of the deposits and on their chemical and mineral composition. Of the purely physical conditions, climate, altitude, and relief are important. Permeability of the deposits is favorable to reprecipitation, for if solutions can not find access to the lower horizons the metals dissolved near the surface may be scattered. The duration of the period of weathering is important also, for under certain conditions the amount of leaching and reconcentration is directly proportional to the time during which the deposits are exposed to weathering. Indeed, there is scarcely a feature of the geologic history of a deposit that may not affect the extent and character of its enrichment.

CLIMATE.

TEMPERATURE.

A warm climate, in so far as it favors chemical action, is favorable to enrichment. Deposits in high latitudes are not so likely to show extensive migration of the metals, because low temperature decreases chemical activity and freezing prevents solution. Where the ground is frozen to considerable depths during the winter and thaws out only a short distance below the surface during the summer, thorough weathering can not extend to great depths. Assuming the persistence of the present relation between latitude and climate, it may be said that bonanzas of secondary ore are less numerous and less extensive in higher than in lower latitudes.[1]

In late geologic time large areas in northern latitudes have been glaciated, and in many places the surface has been planed off by ice erosion. The altered zones of many deposits have doubtless been removed. Thus the deposits of the North differ from those of lower latitudes in two essential respects—in environment and in geologic

[1] Winchell, H. V., Prospecting in the North: Min. Mag., vol. 3, pp. 436–438, 1910. Brock, R. W., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, pp. 24–205, 1911.

history. To what extent the smaller development of secondary sulphide ores in the North depends on present temperature and other climatic conditions, and to what extent it is due to recent glacial action, are questions that probably will not be answered until more data are available concerning deposits in driftless areas in high latitudes. In Alaska, Canada, and New England there are but few sulphide deposits of proved secondary origin that are comparable in extent or value to those which have formed at lower latitudes. The available evidence indicates that the large and important ore bodies of these countries are mainly of primary origin. The gold deposits of Douglas Island, Alaska; the copper deposits of Kasaan Peninsula, Latouche Island, and Prince William Sound; and the nickel and copper deposits of the Sudbury region are not deeply oxidized. Carbonate ores extend to a depth of 300 feet in the Copper Mountain mines, Prince of Wales Island, and chalcocite and native copper lie at least 200 feet deep at the Goodro mine.[1] In many of the deposits in the North, however, the ore has proved to be of approximately uniform grade to considerable depths.

On the other hand, it is well known that great climatic changes have taken place in many regions, and that temperatures have been by no means constant throughout geologic time. Therefore, because the processes of weathering of ore bodies are slow to-day in certain places, it does not follow that they have always been inactive there, and under favorable conditions secondary deposits formed in older geologic periods in places protected from erosion should be preserved to-day.

The rich native silver ores of Cobalt, Ontario, have been considered secondary by some investigators, but all who have studied these deposits are not agreed as to their genesis.[2] Doubtless some enrichment has taken place in the Copper Cliff and Vermilion mines of the Sudbury region, Ontario. In the Vermilion mine, according to Barlow, native copper, probably derived by alteration from chalcopyrite, is found 900 feet below the surface.[3] In general, the secondary sulphide zones of deposits in western Canada in about the same latitude as these are not extensive, but some deposits—for example, those in the St. Eugene mine, in British Columbia—show unmistakable evidence of sulphide enrichment. The developments in southwestern Canada are not sufficient to permit decisive statements.

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[1] Wright, F. E. and C. W., The Ketchikan and Wrangell mining districts, Alaska: U. S. Geol. Survey Bull. 347, 1908. Wright, C. W., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, p. 359, 1911.

[2] Miller, W. G., Notes on the cobalt area: Eng. and Min. Jour., vol. 92, pp. 645–649, 1911. Emmons, S. F., Types of ore deposits, San Francisco, p. 140, 1911.

[3] Barlow, A. E., The nickel and copper deposits of Sudbury, Ontario: Canada Geol. Survey Ann. Rept., vol. 14, pt. H, p. 106, 1904.

In temperate and torrid climates iron, aluminum, and nickel ores are formed by the weathering of rocks containing those metals. The data available indicate strongly that these processes are not so effective in very cold climates, yet deposits that are now in fairly cold temperate climates show extensive segregation. In northern Minnesota, in the Mesabi range, where the average annual temperature is at present 37° F., weathering of ferruginous sediments has yielded deposits of iron that are probably the most valuable in the world. In the Gogebic range, in Michigan, thorough oxidation and segregation of iron oxides by weathering extends to depths below 2,400 feet. These are perhaps the most deeply oxidized deposits in the Western Hemisphere. The Lake Superior iron ores have been exposed to weathering since pre-Cambrian time, and in this long period much concentration has taken place. Moreover, the climate in northern latitudes was probably once warmer than it is now. Deposits that were formed under torrid or temperate conditions are likely to be found in the far North. There is doubtless a relation between latitude and superficial enrichment, but it is one that can not be expressed by an invariable rule.

On the other hand, many sulphide deposits in lower latitudes do not show sulphide enrichment. Examples are mines lying in the foothill copper belt, California (see p. 233); La Reforma mine, Mexico (p. 242); the Copper Queen mine, Velardeña, Mexico (p. 244); and several deposits of the Braden Copper Co., Chile (p. 247). According to J. M. Moubray,[1] several deposits in the Kafue copper district, in northern Rhodesia, between 13° and 14° south of the Equator, show copper sulphides at the very surface. In the Sable Antelope mine of this region superficial alteration is practically absent.

RAINFALL.

Since water is the agent of ore enrichment, abundant rainfall is favorable to the formation of secondary ores. The activity of ground water depends principally, however, on the natural acids and other compounds which it dissolves, and the waters in regions of oxidation and solution are generally not saturated with acids. Thus, even in arid regions a moderate supply of ground water under conditions favorable to permeability may bring about appreciable results in relatively brief geologic periods. Some of the silver-gold deposits of the Great Basin clearly show deep alteration and sulphide enrichment, although the primary ores were deposited as late as or later than the Miocene epoch. Ores that form some of the best examples of sulphide enrichment seen in the United States are found in

[1] Moubray, J. M., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, pp. 117–118, 1911.

deposits that occur in the arid Southwest, where the annual rainfall is not more than 10 or 12 inches. In some of these deposits, however, much of the secondary ore was probably formed when the rainfall was greater. Concerning this point it is obviously difficult to draw any general conclusions, because data regarding the former climates of many arid regions are inadequate.

In arid countries the ground-water level is likely to lie deep, and the zone of solution is generally not clearly differentiated from the zone of precipitation. Above the water level in ore deposits in arid regions there may be considerable amounts of primary sulphide ore, of secondary sulphide ore, and of oxidized ore, all at approximately the same horizon. In such deposits the secondary sulphide ores, though occurring through greater vertical ranges, may not be concentrated in small volume.

ALTITUDE.

As a rule, relief is great in areas of high altitudes, and erosion is consequently more rapid. Moreover, in such areas temperatures are lower and conditions are less favorable to solution. Deposits at very high altitudes, where rocks are disintegrated by frost and carried away unweathered as talus and bowlders, are not so likely to be extensively enriched as are deposits at lower altitudes. Because erosion is slower at low altitudes, topographic surfaces in low regions are more stable than those in high regions. Rocks are commonly decomposed more thoroughly at low elevations. Many iron and aluminum deposits of the lateritic or residual type are formed by the thorough decomposition of iron-bearing or aluminum-bearing rocks. The physiographic conditions most favorable to such decomposition are found in regions approaching base-level, where the removal of valueless material can go on for a long time. As a peneplain is eroded very slowly the weathered residual material will accumulate. Nevertheless, many residual ores are found at high altitudes. The Cuban iron ores occur on elevated plateaus, and the residual nickel ores of New Caledonia are found high on the mountains. Many such deposits that are now found at considerable altitudes were doubtless formed at lower altitudes in regions that have subsequently been elevated. Some decomposed surface zones are related to old base-levels or peneplains that were afterward raised.

The processes of sulphide enrichment, on the other hand, are effective under certain conditions at considerable altitudes. Many deposits in Colorado that outcrop at altitudes about 10,000 feet above sea level and some in Montana that outcrop at about 8,000 feet above sea level contain extensive zones of secondary ores.

RELIEF.

In so far as strong relief supplies head, it is favorable to deep and rapid circulation of underground water, and it is likewise favorable to relatively deep enrichment. In base-leveled regions concentration may take place by the removal of valueless material near the surface, as is indicated above, but the underground circulation is sluggish and its nearly stagnant waters can not descend far into the zone of primary ore without losing the valuable metals that they may have dissolved higher up. Calculations made for lodes in the base-leveled region that includes Ducktown, Tenn., show that all or nearly all the secondary copper in the chalcocite zones may be a result of the leaching of the gossan below the old base-leveled surface. Under the conditions that prevailed in that district, at least, it appears that a large part of the copper dissolved and reprecipitated in any secondary sulphide zone that was formed while the country was being reduced to base-level probably had been redissolved and scattered when the country reached base-level. In deposits that were more permeable and in those that had been enriched to greater depths the conditions would have been more favorable to the preservation of the secondary ores formed before base-level had been approached. The available data regarding sulphide enrichment of base-leveled deposits are scant, for nearly all ore deposits that clearly show sulphide enrichment are in areas of moderate or strong relief.

PERMEABILITY.

No rocks are so impermeable as to be unaffected by weathering, but some decompose more rapidly than others. Decomposition is aided by fracturing and fissuring, and for concentration by redeposition, which requires downward migration of metals, permeability is essential. If the primary deposits are not permeable, the solutions that pass downward through the oxidized zones will move laterally along the contact between oxidized and sulphide ores and ultimately will escape into fractures in the wall rock or reissue as springs at some level below the points of entry. If they do not encounter a reducing environment, the metals may be scattered. In rocks that have been shattered by strong movements since the primary ore was deposited there is generally more extensive and deeper enrichment than in deposits that have been but slightly fractured. Brittle minerals, like quartz and chert, fracture readily, and deposits composed largely of the brittle minerals are generally more deeply enriched than deposits of tough or elastic minerals. Many of the heavy silicate sulphide ores of contact-metamorphic origin that carry a gangue of abundant fibrous amphibole, mica, chlorite, or like minerals do not show sulphide enrichment to great depths.

In a great many districts, especially in the western part of the United States, pronounced earth movements have occurred since the ores were formed. Many deposits fill fissures or were formed in zones of fracturing that were planes of weakness along which movements took place before ore deposition. To relieve subsequent stresses the same zones of fracture may be again fractured, like a rod that breaks at or near the place where it was welded. Such later fracturing has taken place in many mineral deposits after the primary ore was deposited, and consequently many of the planes of later movement may parallel the veins, following one wall or the other or cutting irregularly across the ore. If the deposit is composed of material that is easily fractured, such as quartz or chert, the ore may become brecciated and may therefore contain many small openings. A large number of small openings, such as may result from fracturing or shattering of the primary sulphides, are more favorable to concentrated enrichment than a few larger openings, for a larger surface of primary ore is exposed to solution along many small openings than along a few large openings. Moreover, inasmuch as friction is greater along small openings, the descent of solutions in them is retarded, and therefore reactions that result in precipitation of secondary sulphides may be brought nearly to completion at relatively shallow depths.

As stated above, even the most solid rock will ultimately succumb to surface weathering. Rocks that have long been exposed at the surface, even those that appear fresh, will under the microscope show characteristic changes. The feldspars will be more or less kaolinized, the ferromagnesian minerals will be altered to chlorite, iron oxides, and other minerals, and the dark micas will be bleached. All these changes show that solid rocks are not altogether impermeable. Some minerals, however, seem to be water-tight; fluid inclusions in quartz are common, and some cavities are occupied by gases under pressure. Examples of fluid inclusions are known even in minerals that have good cleavage. Albite at Zimapan, Mexico,[1] carries fluid inclusions, and cavities from which fluids have been drained have been observed in calcite. Yet these minerals are slowly disintegrated and become permeable, especially in the vadose zone. Very small openings, such as the pore spaces of minerals and other capillary or subcapillary openings, are normally not effective water channels, because friction along them retards circulation. Under some conditions, however, even in the secondary sulphide zone, cold mineral-bearing solutions do penetrate these minute openings and deposit ore in them. In certain deposits near Globe, Ariz., according to

[1] Lindgren, Waldemar, and Whitehead, W. L., A deposit of jamesonite near Zimapan, Mexico: Econ. Geology, vol. 9, p. 455, 1914.

Ransome,[1] specks of secondary chalcocite ore are embedded in solid veinlets of quartz and in silicified schist, indicating a migration of copper, for short distances at least, through exceedingly minute openings. Although water may penetrate such minute openings, it does not circulate freely in them but is nearly stagnant. It would be supposed that the metals would not be carried far in such openings before precipitation, at least not in rocks that are readily attacked by the solutions, but if the openings are lined with siliceous alkali-free minerals or with other minerals that are but slowly affected by the solutions, the reactions which reduce and tend to neutralize the solutions and to precipitate the metals would take place more slowly and the metals might be carried in solution to greater depths.

INFLUENCE OF RATE OF EROSION ON RATE OF ENRICHMENT.

Slow erosion favors the concentration of deposits that are formed at the surface by the removal of valueless material—for example, the concentration of residual iron ore. In so far as strong relief is favorable to rapid erosion it is unfavorable to thorough leaching. Where erosion is slow the outcrops and upper portions of deposits are exposed to processes of weathering for periods long enough to favor through leaching, and, if the metals are reprecipitated at lower depths, to favor sulphide enrichment. On the other hand, erosion may be delayed to a point beyond which it is unfavorable to solution and precipitation. The downward migration of the zone of oxidation exposes new surfaces to solution, making masses of fresh ore available for reconcentration. Consequently where metals dissolve readily, comparatively rapid erosion may favor rapid concentration. The metallic contents of many deposits of secondary ores represent not only what has been leached from the gossan now exposed but also what has been dissolved from portions of the deposits that have been carried away by erosion.

AGE OF THE PRIMARY DEPOSITS AND THEIR PERIODS OF WEATHERING.

Other conditions being similar, the amount of enrichment may depend on the length of time the deposits have been exposed to weathering and erosion. In general, weathering has acted for a shorter time on late Tertiary deposits than on middle Tertiary, early Tertiary, or Cretaceous deposits. The age of the deposit is not, however, invariably the most important factor in determining the extent of its enrichment, for some of the middle or late Tertiary deposits, such as those in the southwestern part of the United States,

[1] Ransome, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, pp. 217–218, 1910.

show more extensive migration of the metals than is shown by some older deposits which have been exposed to weathering for a much longer time.

In the United States the bonanza deposits of the precious metals are in the main the younger ones, for in general the Paleozoic and older deposits are less rich, though many of them are more nearly uniform in value. Many of the middle or late Tertiary deposits of the precious metals in the Great Basin region—such as those of Tonopah,[1] the Comstock lode,[2] and Tuscarora, Nev.—show unmistakable evidence of enrichment, yet there are good reasons for supposing that the primary ores of many of these young deposits were originally somewhat richer nearer the surface than at greater depths. The deposits of Cripple Creek, Colo.,[3] and of Goldfield, Nev.,[4] show a similar relation as to values and depth, yet sulphide enrichment has probably not been appreciably important in either of these districts. Gold is generally slow of solution, especially where the environment is not favorable to solution. As pointed out by Graton,[5] some of the gold deposits of the Appalachian region are workable at their outcrops, where gold has remained undissolved ever since the peneplanation of the region, which probably took place as early as Tertiary time.

In general, the sulphide deposits that show the most clearly defined secondary zones are those of copper. The periods of primary deposition of all the known important copper sulphide deposits of determined age in the United States, except those of Tintic, Utah, probably antedate the Miocene, and all have long been exposed to erosion and weathering. According to Ransome,[6] the deposits at Bisbee, Ariz., may have been exposed to processes of alteration as far back as the Cretaceous. The copper deposits of Velardeña, Mexico, according to Spurr and Garrey,[7] are probably later than middle Tertiary. The deposits of the Braden mine of Chile, as shown by Pope Yeatman,[8] are likewise of comparatively late age. In none of these districts where middle Tertiary or later ores are developed are the secondary

[1] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 95, 1905.

[2] Becker, G. F., Geology of the Comstock lode and the Washoe district: U. S. Geol. Survey Mon. 3, p. 273, 1882.

[3] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 204, 217–232, 1906.

[4] Ransome, F. L., Geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, pp. 191–195, 1909.

[5] Graton, L. C., Reconnaissance of some gold and tin deposits of the southern Appalachians, with notes on the Dahlonega mines by Waldemar Lindgren: U. S. Geol. Survey Bull. 293, p. 67, 1906.

[6] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 160, 1904. Also this bulletin, p. 208.

[7] Spurr, J. E., and Garrey, G. H., Ore deposits of the Velardeña district, Mexico: Econ. Geology, vol. 3, pp. 724–725, 1908.

[8] Yeatman, Pope, The Braden copper mines: Min. and Sci. Press, vol. 103, pp. 769–772, 1911.

sulphide zones conspicuously shown. Many copper deposits of the eastern United States are much older, the more important ones having been formed in Paleozoic or earlier periods. Although some of these deposits have long been exposed to erosion, their secondary sulphide zones, though rich and well defined, are not nearly so deep nor so extensive as some in the younger deposits of the West.

I do not know of any secondary sulphide zones that were unquestionably formed in pre-Mesozoic time, although zones of oxide enrichment as old as the Archean are known. According to Van Hise and Leith [1] some of the rich specular hematites of the Vermilion Range are the metamorphosed products of surface enrichment that were indurated and infolded before the beginning of Algonkian time. In the Marquette range, Mich., surface concentration is known to antedate the Animikie (upper Huronian) rocks.

PALEOPHYSIOGRAPHY.

Inasmuch as enrichment depends on the action of surface agencies, it is important to know as far as possible the details of the history of any deposit considered, the length of time it has been exposed to weathering, and whether faulting or folding or a second episode of primary ore formation has taken place since it was first formed. In short, any geologic or physiographic data might have a bearing on the problem of enrichment.

Residual ores of iron, aluminum, or of other metals that have formed on and just below an ancient peneplain may be lifted up and the plain may be deeply dissected by rejuvenated streams. Side wash in valleys will scatter ore along the slopes and mechanical deposition of material already weathered may take place on the bottoms of valleys. Thus residual ores, where abundant, will tend to veneer new surfaces as they are formed.

The study of the deposition and enrichment of lode ores may give rise to important physiographic problems. If the present topography is like that which prevailed when primary deposition took place—and it may be if the deposits were formed in comparatively late geologic time—then the richer ore of the primary deposits may have an obvious relation to the present surface. In some deposits of gold and silver ore the maximum precipitation of the metals appears to have taken place at relatively short distances below the surface that existed at the time of deposition. Thus the primary ore may show a comparatively constant change in value, which may decrease with increasing depth. In general, the more remote the period of primary deposition the less the probability that the important fea-

[1] Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 142, 1911.

tures of the present topography are similar to those which existed when the primary ores were deposited and the less the probability of error in attributing the deposition of a rich primary zone to secondary processes.

STRUCTURAL FEATURES AND BLIND LODES.

Lodes that do not outcrop are termed "blind" lodes. Some of them do not outcrop because the primary ores did not extend to the present surface, others have been faulted off near the surface, and still others have been covered by formations deposited later than the ores. A fissure across a sedimentary series may end abruptly just below or at a bed of shale, and the ore that fills it will then be exposed only where the shale has been eroded away. The portion of a lode that is now capped by an impervious shale will not have been enriched by oxygenated waters unless, because of certain structural conditions, such waters were conducted laterally below the shale bed to the lode. Such structures as thin saddle reefs, thin anticlines, and thin flat-lying beds are not particularly favorable to extensive sulphide enrichment, because they may be eroded in comparatively short time and because the conditions below the deposits they contain are not likely to be so favorable to precipitation as they are in deposits or in parts of deposits that are underlain by sulphide ores. In the absence of material below that may react with the solutions and readily cause precipitation, the metals are likely to be scattered. Nearly vertical or steeply dipping tabular deposits are in a position favorable for secondary concentration, but sulphide enrichment may be extensive also in large isodiametric deposits, or in thick deposits that stand in any attitude.

Deposits that outcropped at one time but are now covered by sedimentary rocks or by later lava flows may have been exposed to weathering and may have been enriched by oxygenating water before the beds covering them were laid down. It can not safely be assumed that the rich ores below the beds covering such deposits are primary and therefore likely to extend downward to indefinite depths. The secondary zones would obviously be related to a topography that existed long ago and not to the present one.

Systems of postmineral fractures in ore and country rock are structural features of obvious importance in the consideration of the enrichment of any ore deposit.

GLACIATION.

In comparatively late geologic time a considerable portion of North America was capped by a continental ice sheet, which removed by erosion the loose débris and the surface rock over great areas. Glaciation was most extensive in northern latitudes, but the continental

glacier extended southward as far as Ohio and Missouri rivers, and smaller glaciers accumulated in the more lofty mountain ranges of the American Cordillera. Many of the ore deposits that lay in the paths of the glaciers were planed off, and the ores in their upper zones were scattered in the rocky material which was left when the ice had melted. Erratic fragments of such deposits have been carried far from their sources and have been the cause of much fruitless prospecting.

The outcrop of an ore body may be removed gradually by erosion by water, but weathering generally precedes erosion. The solutions may leach the valuable metals from the outcrop and may precipitate them at a lower level, where they will be preserved. But weathering does not attend erosion by ice, and chemical action at low temperatures is slight; consequently the metals present in the portions of the deposits that are removed are likely to be scattered. The extent to which the ore deposits in a glaciated region were weathered or otherwise altered by surface agencies before the glacial period began can not be estimated. The amount of rock removed by the continental ice sheet is known to be considerable, however, for the drift which it deposited is in many places more than 200 feet thick. It is probable that glacial erosion was in places equally great or greater. Whatever the amount of ice erosion, it appears to have been sufficient to remove the highly altered sulphide zones in most parts of northern North America.

As stated already, the processes of solution and enrichment are retarded in regions of low temperature. The areas in which ice erosion has been most vigorous are those in which the lower temperatures prevail to-day, and there is reason to suppose that the deposits in these areas were not so deeply altered before the glacial epoch as were similar deposits at lower latitudes. In Canada and in Alaska there are few large deposits of sulphide ores which are clearly of secondary origin. The sulphide ores now exploited in Canada, except possibly the deposits at Cobalt, in the silver-bearing region of Ontario (which some have considered of secondary origin), and certain well-authenticated examples in British Columbia, are generally believed to be primary. I know of no important secondary deposits in New England. Small deposits of chalcocite ores were exploited in the Ely district, Vermont. In a copper deposit at Milan, N. H., where the sulphides outcrop at the very surface, no considerable amount of oxidation has taken place below 30 feet, and in general oxidation is trivial at even shallower depths. Only a little chalcocite enrichment has taken place, the secondary ore consisting of primary yellow sulphides coated with thin films of chalcocite, adding to its value probably not more than 1 per cent.

In Norway and Sweden, according to Vogt,[1] the surface has been polished clean by the Quaternary ice sheet, and secondary alteration is insignificant.

Glaciers do not erode their beds equally at all places. In their higher portions, where the ice is accumulating, pressures are greater, the ice is more rigid, and erosion is more vigorous. Near the margins, where the ice is melting, deposition exceeds erosion and the deposit of drift protects the surface from wear. These differences are very conspicuous in some mountainous sections of the West, where the glaciers covered only portions of the country and the processes are more clearly shown. In some of the ranges of Montana, Colorado, and Utah, where ore deposits are numerous and varied, the evidences of mountain glaciation are conspicuously preserved. At some places the mountain glaciers seem to have removed very little of the altered ore, for the secondary sulphide zones and even the oxidized ores are intact, and some of these appear to be too extensive to have formed since the Pleistocene or glacial epoch. The Amethyst lode at Creede, Colo., has an extensive secondary zone, and one end of this lode was overridden by the ice in late geologic time. In general, erosion by mountain glaciers has been localized, the maximum wear taking place near the heads of the glaciers.

Erosion by the continental glaciers is also somewhat erratic, for great differences in the effect of the action of ice may be seen in a comparatively small area. In the Mesabi range of Minnesota the hard, fresh country rock is polished clean in places, whereas a few rods away and at but slightly lower elevations thick bodies of cellular, almost powdery iron-oxide ore remain intact. These facts suggest that other important secondary zones may be encountered when the area overridden by the continental ice sheet is more thoroughly developed.

THE UNDERGROUND CIRCULATION.

OPENINGS IN THE EARTH'S CRUST.

As emphasized by Van Hise in his treatise on metamorphism,[2] the outer part of the earth's crust may be divided into three zones, differentiated by character of deformation—an upper zone of fracture, a lower zone of flowage, and a middle zone of combined fracture and flowage. The zone of fracture is near the surface. The openings in the rocks of this zone are comparatively stable because the weight

[1] Vogt, J. H. L., Problems in the geology of ore deposits, in Pošepný, Franz, The genesis of ore deposits, p. 675, 1902.

[2] Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, pp. 187–191, 1904; Principles of pre-Cambrian North American geology: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 1, p. 589, 1896.

of the overlying load of material is less than the crushing strength of the rock. At greater depths, where the differences in the stresses exceed the strength of the rocks, openings, if formed, would almost immediately be closed by pressure. It is estimated that for all but the strongest rocks flowage would begin at depths not greater than 5 or 6 miles, where the weight of the overlying mass is greater than the crushing strength of the rocks, but there are some reasons for extending this estimate of the zone of fracture to even greater depths. This problem has recently been investigated experimentally by F. D. Adams [1] and mathematically by L. V. King.[2] Small holes were bored in cylinders of granite that were inclosed in hollow cylinders of nickel steel. Thus confined, the granite sustained loads of nearly 100 tons per square inch, a load more than seven times as great as that which will crush it at the surface of the earth in the usual laboratory tests. Adams concludes that, under the conditions of pressure and temperature that are believed to prevail within the earth's crust, cavities and fissures may exist in granite to a depth of at least 11 miles and may exist at still greater depths if they are filled with water, gas, or vapor, owing to the pressure exerted by the liquid or gas on their inner surfaces.

Superficial enrichment, however, is probably confined to the upper part of the zone of fracture, and although transfers of certain materials may take place in the deeper zones, these do not come within the scope of this investigation. The deepest bodies of secondary sulphide ores now exposed lie at comparatively shallow depths; most of them less than 1,000 feet below the surface, and nearly all that have been developed lie at depths less than 2,000 feet. The depth at which precipitation takes place depends not only on the rate at which the solutions are carried downward but also on the rate at which they react on the walls of their conduits. Although openings may exist at depths of several miles, they would not become channels of circulation unless they were connected. There is without doubt a tightening of the rocks a few hundred feet below the surface, for, as pointed out by Kemp [3] and by Finch,[4] the lower levels of many deep mines are dry.

THE LEVEL OF GROUND WATER.

The terms "water table" and "level of ground water" are generally used to describe the upper limit of the zone in which the openings in rocks are filled with water. This upper limit of the zone of satura-

[1] Adams, F. D., An experimental contribution to the question of the depth of the zone of flow in the earth's crust: Jour. Geology, vol. 20, pp. 97–118, 1912.

[2] King, L. V., On the limiting strength of rocks under conditions of stress existing in the earth's interior: Jour. Geology, vol. 20, pp. 119–138, 1912.

[3] Kemp, J. F., The rôle of the igneous rocks in the formation of veins, in Pošepný, Franz, The genesis of ore deposits, p. 696, 1902.

[4] Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, pp. 193–252, 1904.

tion is not a plane but a warped surface. It follows in general the topography of the country but is less accentuated. It is not so deep below a valley as below a hill but rises with the country toward the hilltops and in general is higher there than in the valleys. Although the water in the zone of saturation does not move rapidly, it is not stationary. If there is a lower outlet, it will move toward that point. Its movements are slow, however, and it may follow a very circuitous route before it issues again at the surface. It follows the paths of least resistance, and if these are downward the water may sink to great depths before it rises, under pressure, to make its exit at some point which is lower than that at which it first entered the belt of saturation. Thus the water table may be considered a kind of indicator that registers the differences between the loss or leakage of the zone of saturation and the addition from the surface.

As the country is eroded, the water level moves downward and, within certain limits, it changes with the seasons. In dry years it is deeper than in wet years, and in dry seasons it is deeper than in wet seasons. The difference of elevation between the top of this zone in a wet year and in a dry year is normally greater under the hilltops than on the slopes and in the valleys. In deposits where the ground is open the level of ground water probably changes with every considerable rain. Consequently there is a zone that is above ground-water level in dry periods but below it in wet periods, and in moist hilly countries this zone may be of considerable vertical extent. Thus the water table oscillates, though in general it moves downward with degradation of the land surface.

THE VADOSE OR SHALLOW CIRCULATION.

Of the rain that falls on the surface a part is drained off by rills and streams, another part is evaporated, and still another part soaks deep into the ground, passes downward, and is added to the water of the zone of saturation. The zone mentioned under the preceding heading—a zone that lies above the zone of saturation and may be relatively dry during a dry period but soaked with water after a wet period—includes openings which in a relatively dry time are filled with air; consequently the water that soaks into the ground after a subsequent rain or snow is aerated and thus becomes a more active agent of solution. The downward movement of such water toward the zone of saturation has been termed the "vadose"[1] circulation. The depth or thickness of this vadose zone is variable, for its lower limit depends on the variable level of ground water. Near

[1] Pošepný, Franz, The genesis of ore deposits, p. 18, 1902. Pošepný includes in the "vadose" circulation water below the "permanent water level."

permanent streams or lakes and other bodies of water this limit is not much higher than they are. In moist hilly countries its depth from the surface varies from a few feet to several hundred feet. In arid regions, where the rainfall is low and evaporation is rapid, this zone may extend to much greater depths. It is, in the main, a zone of solution; consequently its rocks are open and circulation within it is comparatively rapid.

THE DEEPER CIRCULATION.

The circulation of the water in the belt of saturation depends on the relief of the country and on the number, continuity, spacing, and size of the openings in the rocks. Under hydrostatic head the waters in this zone move to points of less pressure and issue at points lower than those of entry. If the deposit is tight and there are no deep outlets, the principal movement is shallow, following down the grade of the undulating water table. As a rule movement in the deeper zone is much slower than in the vadose zone, because the openings are less abundant and also because they are smaller, so that friction on their walls is greater. Some have maintained that the deeper circulation is fairly vigorous, but so far as may be inferred from the developments of deep mines it appears that the underground circulation, in many places at least, is exceedingly sluggish. The depths to which the solutions descend is a question concerning which there are great differences of opinion. In some rocks, under favorable structural conditions, surface waters are conducted, in porous beds or along fractured zones, several thousand feet below the surface, but in other rocks little or no water is collected at depths of more than a few hundred feet.

The shallowness of the zone of the meteoric circulation has been emphasized by Kemp,[1] Finch,[2] and Rickard.[3] In the copper-bearing region of Keweenaw Point, Mich., the lower ends of several shafts that penetrate many layers of bedded rocks are dry and dusty. One of these shafts is sunk about a mile below the surface, but no water is raised from the deeper levels. At Przibram, Bohemia, no water is raised from depths below 2,500 feet, although the workings extend below 3,500 feet. The water raised in the Dives-Pelican mine, Georgetown, Colo., from the sump, 2,000 feet below the surface, was not greater in quantity than that which was pumped from the mine when the bottom of the shaft was at higher levels. The drainage

[1] Kemp, J. F., The rôle of the igneous rocks in the formation of veins, in Pošepný, Franz, The genesis of ore deposits, pp. 681–809, 1902.

[2] Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, pp. 193–252, 1904.

[3] Rickard, T. A., Water in mines; a theory: Eng. and Min. Jour., vol. 75, pp. 402–403, 589–590, 1903. Also, Waters, meteoric and magmatic: Min. and Sci. Press, vol. 96, pp. 872–875, 1908.

tunnels at Cripple Creek become nearly dry a few years after they are run, indicating that the waters in that area are stored in the funnel of the volcanic complex, which is surrounded by relatively impervious granite and crystalline schists.[1] In the lower levels of deep mines of Butte, Mont., there is very little water except that which flows in from higher levels. In many comparatively deep mines of the arid Southwest no body of standing water has been encountered. At Tintic, Utah, according to Finch,[2] water for drilling is conducted into the mines from the surface. Many deep bore holes sunk in search of oil and water have proved to be dry. These and many other examples indicate that the water circulation is exceedingly sluggish in some regions a short distance below the surface.

On the other hand, it should be noted that large volumes of water were lifted for considerable periods from deep levels of the Comstock lode, of the Granite-Bimetallic mine in Montana, of the Commodore mine at Creede, Colo., and of a great many other mines that have been developed more than 2,000 feet below the surface. From this it appears that local differences in the underground circulation are extreme. The amount of fracturing of the deposits, and especially the size of the openings, seem to be the most important factors controlling the rate of the circulation. Friction that retards flow multiplies with decrease in size of channels.

THE REGION OF NEARLY STAGNANT WATERS.

The zone of the deeper circulation differs greatly in depth and vertical extent. Its water is discharged at points that are not lower than the lowest elevation of the country, and if numerous points of discharge are located along a lode that outcrops at several different elevations there will be a considerable lateral movement of the waters toward these, for the solutions move to points of less pressure. If lower rocks are saturated and their openings are filled, the solutions descending from above will find any lateral outlet that is available. In some deposits the solutions doubtless descend to points lower than the lowest outlets and rise again to issue at such outlets, but such circulation is probably slight compared to the circulation that keeps closer to the surface owing to the nearness of points of issue which are located at the surface. Where there are structures that afford passages like inverted siphons there may be a considerable movement of water below the lowest outlet, but under conditions

[1] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 238, 1906.

[2] Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, p. 216, 1904.

of fairly regular spacing of openings along the lode the circulation becomes less and less vigorous as depth increases below the lowest outlet. There is thus a division, probably everywhere somewhat indefinite, between the sluggish deeper circulation and a zone of static or nearly stagnant waters below it. This conception has been clearly developed by Finch in his paper on the circulation of underground waters.[1] There is much evidence that in some rocks the top of this zone lies within a few hundred feet of the surface or even less, but where there are deep open fissures it may be much deeper. Finch cites considerable evidence to show that rocks are generally dry below depths of 1,000 or 1,500 feet, except where they are strongly fractured. Long dry crosscuts, so familiar to all who have worked in deep mines, point clearly to this conclusion.

Other evidence not less convincing may be cited to show that the deeper waters at many places are nearly stagnant. In some of the lodes of the Keweenawan copper country, Michigan, the waters are fairly abundant and are very dilute near the surface[2] and contain principally lime carbonate. At greater depth the freshly opened faces are nearly dry, but at still greater depths—that is, at levels 1,000 feet or more below the surface—the rocks are moist with a concentrated solution of sodium chloride and other chlorides. Lane has called these solutions "connate" waters, and he shows that they are without much doubt residual sea waters which have remained in the rocks since they were formed, or since pre-Cambrian time. In this region, at least, there can not then have been a deep meteoric circulation, for it would have carried fresh water to these rocks long ago. More recently, supporting this conclusion, Lane[3] has cited numerous other examples, in rocks not disturbed, of moderately concentrated waters, probably ancient and connate.

It should be recalled, however, that in the Keweenaw region the circulation may be more active along open fissures, where any residual waters are likely to be dilute. The Challenge exploration of the St. Mary's Mineral Land Co., Michigan, has shown, as is pointed out by Lane, a rapid decrease in the mineral content of the ground water along a level toward a fault.

That the higher concentration of the deep-lying solutions in these tight and undisturbed rocks is due not merely to more active solution of the material of the deeper rocks themselves is suggested by the results of studies by Hodge,[4] who found that the mineral con-

[1] Finch, J. W., op. cit., p. 209.

[2] Lane, A. C., Michigan iron mines and their mine waters: Canadian Min. Inst. Jour., vol. 12, p. 114, 1910.

[3] Lane, A. C., Mine water composition as an index to the course of ore-bearing currents: Econ. Geology, vol. 9, p. 239, 1914.

[4] Hodge, E. T., The composition of waters in mines of sulphide ores: Econ. Geology, vol. 10, pp. 136–139, 1915.

tent of waters in deep openings, like those in mine workings, decreases greatly where horizons of the neutral or alkaline waters are encountered as the depth increases.

PULSATING MOVEMENTS OF UNDERGROUND WATERS.

The underground circulation of water is normally downward from the top of the vadose zone to the water table; thence by less direct routes to greater but generally undetermined depths below the water table; after that laterally, and perhaps upward, to openings that are lower than the points of entrance. This circulation, however, is not to be regarded as a uniform, steady flow. Many springs, probably most of those that are fed by underground meteoric waters, issue more copiously during and immediately after rainy seasons than during dry seasons. At times of droughts some of them will cease to flow. There are sound reasons for supposing that the normal movement of ground water is not steady, even at depths below the ground-water level. After a rainy season the water level is raised and the additional pressure on the water in the zone of saturation will cause it to move more rapidly to points of less pressure and to issue at any available openings. The water that during a dry season has ceased to issue through springs or other openings but has remained nearly if not quite static will have had a longer time to be attacked by ores and gangue minerals with which it is in contact. At depths where air is excluded acid will be neutralized, and as nearly all rocks give alkaline reactions with water the solutions will tend to become alkaline. Higher up, at and above the water level, where air has access, the solutions will be acid. But after a season of heavy rains the acid water of the higher zones will rapidly encroach upon, mingle with, and tend to crowd out the alkaline waters below, which, of course, issue at the surface where openings are available. Thus we may with good reason assume that certain parts of zones of alteration are alternately in alkaline and in acid environments.

WEATHERING OF ROCKS.

All rocks exposed near the surface to water and air are gradually decomposed and broken up. The term weathering includes all those processes that attend such changes. Rain water carries some carbon dioxide, which renders it a more active solvent; if it enters the soil it gathers organic compounds, and some of these will aid solution. Changes of temperature, frost, vegetation, and other agencies loosen the rocks and make them more permeable. The alkalies are readily dissolved, especially sodium. Alkaline earths are attacked also, and calcium and magnesium go into solution. The alkalies render the

solutions still more active solvents. Iron and aluminum are slowly dissolved, the iron more readily than the aluminum. New minerals are formed, especially oxides, hydroxides, and carbonates; but most carbonates are unstable under conditions of thorough weathering.

As a rule the weathering[1] of igneous rocks will increase volume where expansion is possible, but this increase is only temporary, for by solution material is removed. Most ores that have been concentrated by weathering are characterized by much pore space, due to removal of material by solution. The pore space in many weathered rocks equals as much as 50 per cent. But development of pore space weakens the rock, and the pore space may be reduced by slumping. Weathering takes place mainly above the water level. Where rocks are attacked the disposition of products that go into solution may be unimportant economically; where sulphide ores are attacked the disposition of solution products and their precipitation below the vadose zone as "secondary" ores may be of the highest importance.

Of the minerals attacked by weathering, some are comparatively stable: Gold, platinum, chromite, garnet, cassiterite, rutile, monazite, and several other species are not readily attacked, and will accumulate in residual bodies and placers. Quartz is not strongly attacked, but the alkali, alkali earth, and ferromagnesian minerals are more readily dissolved. It may be stated as a general rule that the lower silicates—that is, those containing low silica, like olivine or enstatite—will be changed more readily than feldspars, and the feldspars more readily than quartz. Consequently the basic rocks, such as gabbro and peridotite, are more easily altered. Such rocks are the sources of many metalliferous products of weathering. Kaolin, bauxite, and limonite are stable under surface conditions, and rocks composed of these minerals are but slowly attacked. Iron and aluminum in rocks will enter new combinations, particularly kaolin and limonite.

Air is approximately nitrogen, 77.9 per cent; oxygen, 21 per cent; argon, 1 per cent; carbon dioxide, 0.03 per cent. In rain water oxygen and carbon dioxide are concentrated. According to Bunsen[2] the gases of cold rain water include nearly 3 per cent carbon dioxide and about 34 per cent oxygen. A little chlorine is also present in rain water, but generally only a few parts in a million. Many silicates digested in water give alkaline reactions. Digested with water charged with carbon dioxide, the loss is very appreciable.[3] Thus a powder of potash feldspar (adularia) lost 0.328 per cent in seven weeks. The following table shows the percentage of certain oxides

[1] Merrill, G. P., Principles of rock weathering: Jour. Geology, vol. 4, p. 718, 1892.

[2] Bunsen, R. W., Annalen Chemie u. Pharmacie, vol. 93, p. 48, 1855.

[3] Müller, R., K.-k. geol. Reichsantalt Jahrb., vol. 27, Min. Mitt., p. 25, 1877, cited by Clarke, F. W., U. S. Geol. Survey Bull. 616, pp. 478–479, 1916. The original is not accessible to me.

lost by six minerals when immersed in carbonated water for seven weeks. The column headed "Sum" expresses the percentage of the mineral that went in solution:

Material extracted from minerals by carbonated water (after R. Müller).

	SiO_2.	Al_2O_3.	K_2O	Na_2O.	MgO.	CaO.	P_2O_5.	FeO.	Sum.
Adularia	0.1552	0.1368	1.3527	.....	.....	.....	.....	Trace.	0.328
Hornblende	.419	Trace.	Trace.	.....	.....	8.528	.....	4.829	1.536
Magnetite	.....	.....	.....	.....	.....	.....	.....	.942	.307
Apatite	.....	.....	.....	.....	.....	1.606	1.417	.....	1.529
Olivine	.873	Trace.	.....	.....	1.291	.....	.....	8.733	2.111
Serpentine	.354	.....	.....	.....	2.649	.....	.....	1.527	1.211

Summarizing the weathering processes, Clarke says:[1]

The effect of rain water upon a rock must now be divided into several phases. First, it partially dissolves the more soluble minerals, with liberation of colloidal silica and the formation of carbonates containing lime, iron, magnesia, and the alkalies. The iron carbonate is almost instantly oxidized, forming a visible rusty coating or precipitate of ferric hydroxide. The lime, magnesia, and alkali salts remain partly in solution, to be washed away, together with much of the dissolved silica. * * * The second phase of the process is represented by a hydration of the undissolved residues. The feldspars are transformed into kaolin, the magnesian minerals into talc or serpentine, the iron * * * becomes essentially limonite, and the quartz grains are but little if at all changed. This double process of solution and hydration is accompanied by an increase of volume, which may or may not assist in effecting disintegration. On the surface, the weathered rock crumbles easily; but if the alterations have taken place at considerable depths the pressure due to expansion may hold all the particles in place and the rock will seem at a first glance to be unaltered. Such a rock, although apparently solid when it is first exposed to the air, rapidly falls to pieces and becomes a mass of sand and clay.

The following table gives the results of analyses of diorite from Albemarle County, Va.[2]

Analyses of fresh and altered diorite, by G. P. Merrill.

	A	B
SiO_2	46.75	42.44
Al_2O_3	17.61	25.51
Fe_2O_3	16.79	19.20
FeO		
MgO	5.12	.21
CaO	9.46	.37
Na_2O	2.56	.56
K_2O	.55	.49
Ignition	.92	10.92
P_2O_5	.25	.29
MnO	.....	.....
	100.01	99.99

A is the fresh rock, B its altered equivalent. The concentration of aluminum and iron and the loss of lime, magnesia, and soda are

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, pp. 481–482, 1916.

[2] Merrill, G. P., Rocks, rock weathering, and soils, pp. 224–225, 1906; cited by Clarke, F. W., op. cit., p. 488.

noteworthy. The large loss on ignition of the altered rock indicates extensive hydration during weathering.

In the second table are shown (A) an analysis of elæolite syenite, composed of nepheline, diopside, ægerite, magnetite, biotite, etc., of Fourche Mountain, Ark.,[1] and (B) an analysis of the same rock decomposed.

Analyses of fresh and altered elæolite syenite.

	A	B
SiO_2	59.70	50.65
Al_2O_3	18.85	26.71
Fe_2O_3	4.85	4.87
FeO		
MgO	.68	.21
CaO	1.34	.62
Na_2O	6.29	.62
K_2O	5.97	1.91
Ignition	1.88	8.68
Organic	.....	.....
TiO_2	.....	.06
	99.56	94.33

It is noteworthy that soda is removed more readily than potash. Magnesium and lime are extensively removed. These facts illustrate the principle above noted, that under similar conditions basic rocks will weather more rapidly or more thoroughly than acidic and intermediate rocks. In the concentration of iron and nickel ores by weathering of igneous rocks the basic rocks are of chief importance.

ZONES OF SULPHIDE DEPOSITS.

DOWNWARD CHANGES IN SULPHIDE DEPOSITS.

Residual ores of iron and other metals commonly lie above partly altered rock, below which is generally found the protore or original rock from which the ore has been derived. In the Mesabi range in Minnesota greenalite alters by oxidation to taconite, and taconite, by further oxidation and leaching out of valueless constituents, to rich iron ore. The residual iron ores of Cuba have formed by oxidation and leaching of serpentine, and serpentine probably from alteration of peridotite. Cupriferous iron sulphide ore may alter first to chalcocite and then to limonite (fig. 1). Thus the change from protore to ore or gossan occurs by stages depending on depth, which controls the state of oxidation of the aqueous solutions that are the agents of weathering.

As set forth by R. A. F. Penrose, jr., S. F. Emmons, W. H. Weed, and others, many sulphide deposits show characteristic changes from the surface down the dip. At or near the surface the deposits

[1] Williams, J. F., The igneous rocks of Arkansas: Arkansas Geol. Survey Ann. Rept. for 1890, vol. 2, pp. 81–82; analysis A by W. A. Noyes, B by R. N. Brackett.

are generally oxidized and stained with limonite. The outcrop and the upper part of the oxidized portion of the deposit may be poor. Below this there may be rich oxidized ores; still farther down, rich sulphide ores; and below the rich sulphides, ore of relatively low grade. This lowest ore is commonly assumed to be the primary ore from which the various kinds of ore above have been derived. The several kinds of ore have a rude zonal arrangement, the so-called "zones" being, like the water table, highly undulatory. They are related broadly to the present surface and generally to the hydrostatic level, but may be much more irregular than either, for they depend in large measure on the local fracturing in the lode which controls the circulation of underground waters. Any zone may be thick at one place and thin or even absent at another. If these zones are platted on a longitudinal vertical projection it is seen that the

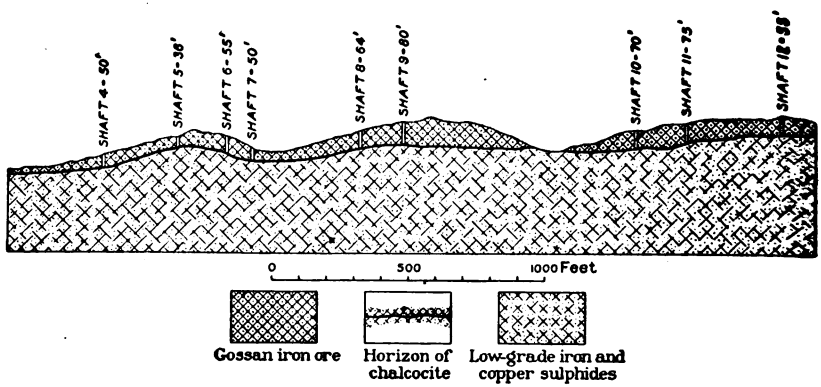

FIGURE 1.—Side elevation of a part of the Old Tennessee-Cherokee lode, Ducktown, Tenn., showing position of secondary or enriched chalcocite ore and of the barren gossan iron ore. In this district the secondary copper ore is exceptionally thin. After W. H. Emmons and F. B. Laney.

primary sulphide ore may here and there project upward far into the zone of secondary sulphides, or into the zone of enriched oxides, or into the zone of leached oxides, or may even be exposed at the surface. The zone of sulphide enrichment (which is not everywhere present) may project upward far into the zone of rich oxidized ore, or into the zone of leached oxides, or may outcrop at the surface. The zone of sulphide enrichment nearly everywhere contains considerable primary ore, and commonly the so-called secondary ore is merely the primary ore containing in its fractures small seams of rich secondary minerals. The zone of enriched oxides is generally found above the lowest level reached by the water table. This zone in places extends to the outcrop. The zone of secondary sulphides in moist countries is in general below the water level. In arid countries it may be partly or entirely above the water level.

All these zones except that of the primary ore are, broadly considered, continually descending. Ore taken from the outcrop may represent what was once primary ore; afterward, enriched sulphide ore; still later, oxidized enriched sulphide ore; later still, leached oxidized enriched sulphide ore; and finally it became the surface ore or gossan. Through more rapid erosion at some particular part of the lode any one of these zones may be exposed, and hence an outcrop of ore of any character is possible.

THE OXIDIZED ZONE.

CONDITIONS IN THE OXIDIZED ZONE.

In the presence of air and water ores and protores break down and form soluble salts and minerals that are stable under surface conditions. Silicate rocks and carbonate rocks are altered and commonly change to residual ores of iron, aluminum, and other metals, the nature of the ore depending on the composition of the rocks and the thoroughness of weathering. Sulphide ores also are altered. No metallic sulphide that is long exposed to the action of these agents remains unchanged. Iron sulphides, which are present in practically all deposits of sulphide ores, are altered to iron oxides, and such a change is attended by the liberation of iron sulphates and sulphuric acid, which under favorable conditions dissolve many of the minerals. In many deposits relatively stable basic iron sulphates are formed, but even these eventually break down.

The oxidizing zone is in the main the zone of solution. Precipitation also takes place in this zone, especially the precipitation of the oxides and hydrous oxides of iron, aluminum, manganese, and silicon. By redeposition deposits of the more valuable metals are formed also in this zone. Solution generally exceeds precipitation, however, and by solution the mass is reduced and open spaces are enlarged. In limestones many of these spaces, called "watercourses," are large enough for a man to pass through. The increase in the size and in the volume of the openings renders the downward circulation comparatively free in the zone of oxidization. Regarding the processes of solution at Bisbee, Ariz., where oxidized ores are exceptionally developed, I quote the following from Ransome:[1]

> The most marked physical effect of the oxidation of the ore bodies has been a great increase in the porosity of the masses acted upon. This, by enabling solutions to percolate easily through the partly oxidized zone, has greatly facilitated the migration and concentration of the desulphurized ores and their segregation in workable masses from the bulk of the limonitic and clayey "ledge matter."
>
> The oxidized material is not only more porous but much softer and more plastic than the original mineralized limestone and hence greatly weakens by

[1] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 159, 1904.

its presence the rocky structure in which it occurs. The overlying limestones, no longer adequately supported, fissure and settle down upon the soft plastic ore and gangue. The access of solutions is thus still more facilitated, and the processes of oxidation and solution proceed so much the faster. That part of the surface which is underlain by oxidizing ore bodies is thus rendered less resistant to erosion, other things being equal, than the surrounding country.

Some of the metals—for example, gold—dissolve very slowly in the zone of oxidation. If the other materials in an ore deposit are taken away the ore may be enriched by decrease in volume, in the manner elucidated by Rickard.[1]

The hydrous oxides, once formed, are comparatively stable, and under certain conditions the more valuable metals dissolve more readily than the other vein materials in the oxidized zone. Consequently the oxidized zones may be leached of the valuable metals. Leaching is generally incomplete, however, for owing to the removal of the outcrops by erosion, new surfaces are presented to attack.

As already stated, the oxidized zone is generally above a secondary sulphide zone. As the latter is the richest part of many sulphide deposits, and as the zone of oxidation is descending, the processes of oxidation attack materials that are comparatively rich. In many deposits the first effect of oxidation is to convert the richer sulphides to rich oxides; consequently the lower part of the oxidized zone may be as rich as or even richer than the secondary sulphide zone.

As copper sulphides may replace iron sulphides almost completely in the altered zones of some deposits the gossans in such regions represent the oxidation product of a chalcocite zone nearly free from iron. Thus the outcrop may be only slightly stained with iron. Some important bodies of copper ores at Butte, Mont., at Morenci, Ariz., at Bingham, Utah, and at Cananea, Mexico, have outcrops composed of light-colored kaolinized rocks that are not highly ferruginous.

SEGREGATION OF THE METALS IN THE OXIDIZED ZONE.

As a result of surface alteration the metals are at many places segregated in the oxidized zone. Low-grade protores of iron silicates and iron carbonates become rich ores by weathering. In sulphide deposits the changes are not less marked. At Ducktown, Tenn., a pyritic copper ore is converted near the surface into a high-grade iron ore. Below the iron ore is an exceptionally rich chalcocite ore, and below this the low-grade copper ore, the original deposit from which the iron ore and the rich copper ore have been derived. At Ducktown, as in many other districts, the processes of alteration are

[1] Rickard, T. A., The formation of bonanzas in the upper portions of gold veins, in Posepný, Franz, The genesis of ore deposits, pp. 734–755, 1902.

clearly related to the water level, which divides the zone of solution from the zone of precipitation of copper, but in certain districts where the water level is lower nodules of oxidizing ore show the same zonal arrangement. Many of these nodules or spheres are made up of successive shells, each inclosing a smaller one, like the layers of an onion. Although the spherical shape of some of these nodules may be original, most of them have become rounded by oxidation. Where irregular blocks are inclosed by fractures to which water and oxygen have access, processes of oxidation, extending inward from the fractures to approximately equal depths, tend to round off irregularities of the unaltered mass, because the inequalities are the more exposed. The processes may be compared to concentric weathering at the surface.

At the Southern Cross mine, near Cable, Mont., nodules of gold-bearing pyrite are surrounded by shells of limonite which clearly have been derived from the oxidation of the iron sulphide in place. Gold is concentrated in the outer shells by diminution of mass, but volume for volume the tenor of the iron sulphide and iron oxide is approximately the same. At Leadville, Colo., according to Ricketts,[1] nodules of galena carry six times as much silver as the cerusite crusts that surround them. A number of assays cited by S. F. Emmons[2] show a silver content of 420 ounces per ton of galena and only 28.6 ounces per ton of the corresponding cerusite crusts. In view of the fact that the galena of Carbonate Hill averages only 145 ounces per ton,[1] these figures seem to indicate addition of silver to the galena, as well as leaching of silver from the carbonate.

To illustrate the separation of copper and iron in the zone of oxidation, I quote from Lindgren, Graton, and Gordon[3] the following description of oxidizing nodular masses in the Apache No. 2 mining district, New Mexico.

> The primary ore consists here of a gangue of extremely coarse calcite with a little iron and practically no magnesia. When this is dissolved in acid there remains a skeleton of small films and grains of quartz whose presence would hardly be expected in the apparently homogeneous cleavage pieces. The calcite contains grains of chalcopyrite and small cubes of pyrite. During oxidation this primary low-grade ore becomes surrounded by crusts of secondary calcite, limonite, hematite, malachite, and chrysocolla. The iron and copper separate, the former being deposited in the recrystallized calcite as hydroxide or oxide, while the copper minerals form a thin crust directly adjoining the primary ore and gradually traveling inward as the oxidation progresses. This is exactly what happens under the more intense conditions of artificial oxidation or the

[1] Ricketts, L. D., The ores of Leadville and their modes of occurrence, p. 37, Princeton, 1888.

[2] Emmons, S. F., Geology and mining industry of Leadville, Colo., with atlas: U. S. Geol. Survey Mon. 12, pp. 553–554, 1886.

[3] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 55–56, 1910.

roasting of chalcopyrite in metallurgical work. The heat in the presence of oxygen will gradually concentrate the copper sulphide or oxide in the center of the lump, while the ferric oxide forms a shell which can easily be knocked off.

Considered in more detail, the narrow ring of oxidized copper ore consists of alternate narrow bands of malachite and chrysocolla, the latter being due to the quartz distributed microscopically through primary calcite. The malachite always forms the inner zone and projects into the fresh calcite as tufts of slender needles. In places a thin layer of calcite will separate the copper minerals. The wide outer crust consists of recrystallized calcite which only in part has the same orientation as the central cleavage piece of primary ore. This recrystallized calcite contains limonite in flocculent masses, in places distributed concentrically, but does not carry even a trace of copper. At the outer edge of the specimen the limonite changes to dark-brown hematite.

At Bisbee, Ariz., the segregation of the metals in the zone of oxidation is shown on a grand scale. As stated by James Douglas,[1] a large mass of ore developed between the 200 and 400 foot levels of the Copper Queen mine consists of a core of compact pyrite, very lean in copper, surrounded by a shell of rich copper ore. According to Ransome,[2] a mass of pyrite was noted on the 1,000-foot level of the Lowell mine, lying generally parallel with the bedding of the limestones and in contact with partially oxidized ore both above and below. Some native copper was seen in the oxidized ore close to the pyrite. Similar residual masses of worthless pyrite surrounded by good ore, usually containing chalcocite, were seen on the 1,050-foot level of the Calumet & Arizona mine.

The processes that operate to form the small nodules are probably similar to those that operate to form the larger masses. Many details of the chemistry of these processes have not been worked out, but it is known that oxidation favors the solution of some compounds and the precipitation of others. Dilute acid in the presence of air dissolves the sulphides of both copper and iron. Iron but not copper is precipitated by hydrolysis of sulphates. Dilute acid in the absence of air dissolves iron sulphide but not copper sulphide, for copper sulphide is precipitated at the expense of iron sulphide if air is excluded. The spherical bodies of enriched sulphide ore in the zone of oxidation, which are crusted with lower grade, presumably leached oxidizing ore, doubtless illustrate in a small way the same processes that result in the rearrangement of the metals in the several zones that are related to depth.

The separation of lead carbonate and zinc carbonate during the oxidation of ore bodies containing zinc and lead sulphides is conspicuously shown in some districts, especially in ore bodies inclosed in limestone. At Leadville, Colo., deposits of sphalerite, galena, and

[1] Douglas, James, The Copper Queen mine, Arizona: Am. Inst. Min. Eng. Trans., vol. 29, p. 531, 1900.

[2] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 146, 1904.

pyrite are overlain by large oxidized ore bodies, some of which consist of argentiferous cerusite containing but little zinc and others of iron-stained smithsonite containing little lead. At some places a zone of smithsonite is below one of lead carbonate. At the Kelly mine, in the Magdalena district, N. Mex., these processes have taken place on a smaller scale but are very clearly indicated. There, according to Lindgren, Graton, and Gordon,[1] the primary ore consists of zinc blende, magnetite, a little pyrite, and galena. As stated by these investigators—

> The depth of oxidation is about 300 feet. * * * In the oxidized stopes nearer the surface the zinc and lead part company. The oxidized zinc ores form wide stopes in which caves large enough for a man to crawl into are coated with beautiful botryoidal, light-green masses of smithsonite. The crust of this material is almost 3 inches thick, and underneath is a dark powdery material rich in manganese but also containing much zinc. The lead stopes are much smaller and are composed of almost pure "sand carbonate" with occasional bunches of galena.

DEPTH OF THE OXIDIZED ZONE.

The depth of the zone of oxidation and the extent of oxidation within that zone depend upon the permeability of the ore and its character and composition. Conditions differ greatly in different districts and even in different deposits in the same district. The depth of thorough oxidation is generally less than the depth of the vadose circulation, for oxidation follows the depression of the water level. Where the ground-water level has been depressed by relatively rapid climatic change rather than by the gradual downward migration of ground water that attends the normal degradation of a country the rate of its depression may be more rapid than that of the zone of oxidation, and in consequence the sulphide ores may be marooned in the vadose zone. In an arid country oxidation is probably slow, for it depends in a measure on the supply of oxygen-bearing waters. Thus at Tonopah, at Morenci, and in some other districts in the Southwest the lower limit of oxidation has lagged far behind the downward-migrating water level.

The depths of oxidation and enrichment of iron-bearing rocks show extensive variations. The iron ores of Mayari, Cuba, formed by decomposition of serpentine, extend to depths about 30 to 40 feet below the surface. In the Mesabi range, Minn., ferruginous sediments are altered to depths of 200 feet and locally as much as 600 feet below the bottom of the drift mantle. In the Cuyuna range, Minn., the ores formed by oxidation are commonly found at depths of 500 feet and locally 1,000 feet. In the Gogebic range, Mich., in

[1] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 55, 1910.

the Newport mine, ores have formed by oxidation at depths below 2,400 feet. This oxidation has been accomplished, moreover, by waters that are practically free from sulphuric acid. A few but not many sulphide deposits show partial oxidation at depths equally great. At Tintic recent developments have exposed oxidized ores about 2,400 feet below the surface. The Old Abe mine, in the White Oaks district, Lincoln County, N. Mex., according to Lindgren, Graton, and Gordon, has been worked to a depth of 1,380 feet, yielding rich oxidized ores.[1] The water level in this mine is 1,300 feet below the surface. In the Brooklyn mine at Bingham, Utah,[2] oxidation is said to extend 1,450 feet below the surface. In the Snowstorm mine, in the Coeur d'Alene district, Idaho, according to Ransome, carbonates of copper are found about 1,200 feet below the outcrop of the lode.[3] At Creede, Colo., partial oxidation has extended locally more than 1,000 feet below the surface.

At Tonopah, Nev.,[4] the depth of oxidation is variable. In veins that outcrop oxidation has taken place locally to depths greater than 700 feet. Veins which do not outcrop but which are capped by volcanic rocks later than the ore show comparatively little oxidation. A single fracture line or a fault line may divide the oxidized from the unoxidized ore and rock. In this district no standing ground water has been encountered in the mine workings, which extend to depths below 1,100 feet.[5]

At Przibram, Bohemia, in a comparatively moist climate, oxidation extends, according to Beck, from 200 to 900 feet below the surface. In some other moist districts, as at Ducktown, Tenn., the oxidized ores are not more than 100 feet below the present surface.

At Butte, Mont., according to Reno Sales,[6] in the vicinity of the St. Lawrence and Mountain View mines, the depth of oxidation is nearly 400 feet, although in many parts of the camp it is only 10 feet. The depth of oxidation in this district depends largely on the composition of the country rock—to a greater degree, in fact, than on the topographic features. The more complete the alteration and pyritization the greater the depth of oxidation. In the central copper area, where the "granite" is strongly altered and pyritized, the upper limit of sulphides is roughly a horizontal plane, although the surface contours in the same area show variations of 300 feet. Over

[1] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 60, 1910.

[2] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 215, 1905.

[3] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, pp. 150–152, 1908.

[4] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 90, 1905.

[5] Idem, p. 96.

[6] Sales, R. H., Superficial alteration of the Butte veins: Econ. Geology, vol. 5, p. 19, 1910.

the remainder of the copper area the average depth of oxidation is approximately 50 feet. The depth of oxidation in the veins is influenced to a slight degree by the physical character of the veins themselves. Under like conditions a quartz vein is oxidized to a greater depth than a fault or "granite vein," owing to the greater impermeability of the clay and crushed "granite" of veins of the latter class.

At Tintic, Utah, where the limit of oxidation in fractured limestone is at least 2,000 feet deep, the ground-water level and zone of unaltered sulphides in igneous rocks scarcely half a mile away is only 200 or 300 feet from the surface.[1]

At Cripple Creek, Colo., partial oxidation is found in some places at depths of 1,200 feet,[2] but in other places it is relatively shallow.

SUBMERGED OXIDIZED ORES.

As already stated, the oxidized ore is generally above the ground-water level, and in arid countries oxidation is seldom complete at depths considerably above that level. In deep mines little smears and veinlets of oxidized material, generally a mixture of kaolin and limonite or of kaolin and manganese oxide, are found at considerable depths. In most countries such veinlets were probably deposited below the water level. As the solutions descend, their acidity is reduced, and some of the metals which may be held in acid solutions would be precipitated by a decrease of acidity.

Extensive oxidation is probably limited to those parts of deposits that lie above the ground-water level at the time of oxidation. In some deposits, however, the ores are extensively oxidized below the water level. According to B. S. Butler,[3] the ores of the Harrington-Hickory mine, near Milford, Utah, are oxidized at least 100 feet below the present water level. Submerged oxidized ores were found also at Tintic and Park City, Utah, and at Eureka, Nev. At Bisbee, Ariz., the depth of oxidized ore ranges from 200 to 1,600 feet and the deeper oxidized ores are submerged. As shown by Ransome (p. 212), the altered ores are related to a tilted pre-Comanche erosion surface rather than to that existing to-day.

Where ore bodies are extensively oxidized far below the ground-water level it is reasonable to infer that the level of the ground water has risen. The amount of atmospheric oxygen that water may dissolve and carry far below the water level is very small (see p. 150)

[1] Tower, G. W., Smith, G. O., and Emmons, S. F., U. S. Geol. Survey Geol. Atlas, Tintic special folio (No. 65), p. 5, 1900. Emmons, S. F., The secondary enrichment of ore deposits, in Pošepný, Franz, The genesis of ore deposits, p. 438, 1902. Lindgren, Waldemar, oral communication.

[2] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 196, 1906.

[3] Oral communication.

and probably would be insufficient to oxidize large masses of sulphides, even in a comparatively long period.

TRANSITIONS BETWEEN OXIDIZED AND SULPHIDE ORES.

In moist countries, where the level of ground water is near the surface, the transition between the almost completely oxidized ore and the unoxidized sulphides is generally abrupt. This is especially noticeable in the pyrrhotitic copper ores of Ducktown, Tenn., where the contact between the two is at some places as sharp as a knife blade. In pyrrhotitic ores of the Encampment district, Wyoming, chalcocite ores occur immediately below the gossan.[1] In the pyritic copper ores of Butte, Mont., according to Sales, the transition is sharp. He says:[2]

> Examined from the surface downward the oxidized portion of a copper vein will show but little variation in physical character or mineral composition between the outcrop and the sulphide ore. The line of separation marking the change from oxidized to sulphide ore is very sharp and clean cut. There is no partial oxidation of the vein; no mixture of sulphides and oxides. The entire change in any single cross section of a vein takes place within 2 or 3 feet vertically. Generally the sulphide ore, through slight changes in the relative abundance of certain minerals, indicates the proximity of the oxides, while in the case of the oxides there is seldom, if ever, any change to indicate a nearness to sulphides. In the copper belt the minor veins, stringers, iron pyrite seams, country rock, etc., are all oxidized and bear the same relation to the surface and to depth of oxidation as do the large veins.

In some other districts, however, there is no such sharp dividing line between the oxide and the sulphide ore. At Bingham, Utah, according to Boutwell,[3] the transition from the zone of oxidation to the zone of sulphide enrichment is gradual, as it is also at Morenci, Ariz., where the zone of secondary sulphides is oxidized through a considerable vertical distance. Says Lindgren:[4]

> The oxidation does not extend down to any well-defined water level, which must be far below the deepest workings, but acts most irregularly, sometimes leaving fresh metamorphic limestone at the surface and again reaching down to a depth of 400 feet along fissures and faults. The present ore bodies probably fell an easier prey to oxidation by reason of their richness in sulphides and their favorable exposure to percolating waters. In such position are the upper ore bodies of the Detroit and Manganese Blue. In other cases the oxidation was facilitated by means of fault planes and porphyry dikes.

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[1] Spencer, A. C., The copper deposits of the Encampment district, Wyoming: U. S. Geol. Survey Prof. Paper 25, p. 55, 1904.

[2] Sales, R. H., Superficial alteration of the Butte veins: Econ. Geology, vol. 5, p. 19, 1910.

[3] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 221, 1905.

[4] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 197, 1905.

At Bisbee, Ariz., the zone of transition between the oxide and sulphide ore is extensive. According to Ransome:[1]

Within the transition zone between completely oxidized and unaltered sulphide ores, which has a maximum depth or thickness of about 900 feet, the oxidizing processes are controlled to a large extent by recent irregular fissuring and by the relative permeability of the various sulphide masses to generally descending solutions. Fissures cutting through masses of lean pyrite are almost invariably accompanied by streaks of rich ore, often containing chalcocite, together with cuprite and native copper. Where there are several such fissures near one another, important ore bodies result. The general association of profitable ore with fissured, broken, permeable ground is well recognized in practical operations and turned to good account in underground exploration.

THE SECONDARY SULPHIDE ZONE.

POSITION AND EXTENT.

The secondary sulphide zone is generally below a zone of oxidation. It is not everywhere developed, not even in copper ores that are capped with gossan. Examples of such deposits are cited on a following page. In many deposits the transition between the oxidized and secondary sulphide zone is sharp, being essentially at the ground-water level. The secondary ores extend downward to various distances below the water level. The vertical extent of the secondary zone differs widely in different districts. In some of the districts of the southern Appalachians the chalcocite zones occupy only a few feet vertically. At Ducktown, Tenn., in all except one mine the average thickness of the secondary chalcocite zone is between 3 and 8 feet, but some secondary chalcopyrite is developed far below this zone. In the East Tennessee mine, in this district, the vertical range of chalcocite is about 125 feet. In the Encampment district, Wyoming, the vertical extent of chalcocite is at least 200 feet. In the disseminated deposits in porphyry at Bingham, Utah, the zone of workable sulphides, mainly chalcocite and chalcopyrite, has an average vertical extent of 418 feet,[2] and, owing to the rugged topography, the vertical range is much greater. At Morenci, Ariz., the belt of maximum deposition of secondary chalcocite is in general from 200 to 400 feet below the surface, although veins of chalcocite are said to extend to greater depths, especially in the Coronado mine. In this mine also, according to Lindgren,[3] chalcocite in places reached the surface. At Bisbee, Ariz., chalcocite, partly oxidized, is found within 200 feet of the present surface and extends to depths at least 1,500 feet below the surface. At Globe, Ariz., in the Old Dominion mine, chalcocite has been found more than 1,200 feet below the surface, and has a

[1] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 145, 1904.

[2] Utah Copper Co. Seventh Ann. Rept., Dec. 31, 1911.

[3] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 210, 1905.

vertical range of at least 800 feet. In the Miami Inspiration ore zone, chalcocite is said to be found 900 or 1,000 feet below the surface. In all these districts chalcocite is regarded as a mineral which is in the main, if not altogether, secondary. At Butte, Mont., chalcocite has been found at depths 2,800 feet below the surface. In the upper levels of the Butte mines secondary chalcocite is abundant, but recent investigations, especially those of Reno Sales, indicate that the chalcocite of the deeper levels is probably primary. At Tintic, Utah, oxidized ore extends to depths of 2,400 feet, and secondary sulphides occur with the secondary oxides. Except at Butte, Mont., and Tintic, Utah, no data now available indicate deposition of secondary chalcocite at depths greater than 1,500 feet below the outcrop. It is not at all improbable, however, that secondary chalcocite deposited at greater depths may be revealed by future exploration.

Examples of enrichment of silver sulphide deposits at depths of 1,000 to 1,200 feet below the surface are well authenticated. In Mexico, at Pachuca, Guanajuato, and Zacatecas, there are several great silver deposits[1] capped by gossan, below which sulphide ores (negros), in part at least of secondary origin, extend downward from 1,200 to 1,500 feet. At lower depths lean pyritic and sphaleritic ores with some galena are found. Possibly secondary deposits of silver occur at greater depths, but it is questionable how far the several species of the silver-bearing minerals may indicate geologic processes. I know of no examples of the precipitation of appreciable amounts of gold by descending solutions at depths more than 1,000 feet below the surface. In general, gold that is dissolved by surface waters is precipitated at relatively shallow depths.

The data reviewed above show that no definite depth can be fixed below which processes of enrichment are not effective. The maximum precipitation occurs at comparatively shallow depths, however, and there is little reason to suppose that these processes are effectively operative in the deeper part of the zone of fracture. The depth to which the metals are carried depends on local climatic conditions, permeability, and the chemical and mineralogic environment.

RELATION TO GROUND-WATER LEVEL.

The ground-water level, the so-called water table, has frequently been regarded as indicating the top of the secondary sulphide zone at the time that zone was formed. As has been stated, the water level is not stationary but oscillates, although it tends to move downward as the major drainage channels approach grade. If the water level

[1] Halse, Edward, On deep mining in Mexico and the changes that occur in the country rock and vein filling in depth: Inst. Min. and Met. Trans., vol. 3, p. 418, 1895.

is comparatively high or if the lode is much fractured, and particularly if it contains large spaces, there is probably but little precipitation of the secondary sulphides above the water level. There are two reasons why this should be true; one is that the solutions descend in open rocks at a comparatively rapid rate through the fractured and partly weathered zone of somewhat cellular ore above the shallow water level, and the other is that several of the sulphides of the more valuable metals that are dissolved readily in an oxidizing environment are not readily precipitated in such an environment. If the rocks are open, atmospheric oxygen should find ready access to the ore above the zone of saturation. Even if precipitation should take place the sulphides precipitated would later be exposed again to oxidation and solution.

The sulphides below the water level are protected from the oxygen of the air, however, and solution of some metals is retarded if not prevented. The solution in sulphuric acid of copper sulphide, silver compounds, and gold requires an oxidizing agent. It is well known that a small concentration of ferrous sulphate, which is surely present in the reducing zone below the water level, will drive gold and silver from solution. Copper sulphide, which dissolves readily in sulphuric acid in the presence of air, is not dissolved in its absence. Hydrogen sulphide is generated by the action of acid on several sulphides and in the presence of the faintest trace of hydrogen sulphide, copper sulphide is not dissolved—not even in boiling concentrated acid.[1] Thus it would be supposed that under these conditions the solution of copper, silver, and gold would be inhibited at ground-water level or a short distance below it. Since a liter of water can absorb under surface conditions only about 6.84 cubic centimeters of atmospheric oxygen, the amount carried dissolved, even in a saturated solution, can not be great. Any oxygen that is made available by hydrolysis when ferric sulphate is reduced to ferrous sulphate and that which combines to form the higher oxides of manganese might delay reduction, but the delay would be only temporary. Although oxygen is required for the solution of gold, silver, and copper, the sulphides of zinc and at least some of the sulphides of iron might be dissolved at depths considerably below water level, for they are attacked by sulphuric acid even in the absence of an oxidizing agent.

Many deposits of secondary sulphide ore in the arid Southwest are well above the present ground-water level. The lower limits of some of these deposits have been reached by mining, and below some of them lie considerable bodies of pyrite and chalcopyrite ore which have been penetrated by mine workings that encountered no standing underground water. As has been already stated, the climate in this

[1] Allen, E. T., oral communication.

area has changed from humid or subhumid to arid in comparatively recent time, and it is possible that some bodies of secondary sulphide ore have been marooned by the rapid descent of the ground-water level that attended the change. At Morenci, Ariz., nearly all the mines are dry in and below the chalcocite zones of the deposits. Of these Lindgren[1] says:

> Chalcocite perhaps forms at the present time in the upper levels of the belt occupied by this mineral where copper-sulphate solutions from oxidizing chalcocite above are abundant and free oxygen absent. * * * Direct oxidation has, in fact, already penetrated to the deepest levels attained in the pyritic zone; at present it works here chiefly along fissures and seams but is probably slowly spreading.
>
> I regard the chalcocite zone as formed about an ancient water level, much higher than the present. During the epoch of the Gila conglomerate the water level was surely at least several hundred feet higher than it is now, and it was probably still higher during Tertiary time, in which a moist climate most likely prevailed.

PRECIPITATION OF SULPHIDES ABOVE THE WATER LEVEL.

In arid districts, where the water level lies very deep, the descending metal-bearing solutions may encounter a reducing environment in the so-called vadose zone, especially in rocks that contain only minute openings, through which the water soaks downward from the surface, excluding the admission of any considerable amount of air. It would be supposed that the oxygen present in such waters and in the imprisoned air would be used up before the descending solutions encountered any zone of permanent saturation, or that before reaching ground-water level the solutions might become reduced, so that the metals could readily be precipitated.[2]

Any former water level doubtless maintained the usual relation to the topography that existed when it prevailed, and it is generally untenable to assume that the topography which controlled a former water level in a region where the climate has changed recently was very different in its major features from the present topography. Stope sheets and other available information show that many of the chalcocite zones in copper deposits of arid regions have a pretty definite relation to the major features of the present topography, and it therefore seems possible that when they were formed they bore the usual relation to the water level then prevailing. The disseminated chalcocite ores of Miami, Ariz., are, however, not definitely related to the present topography, which was apparently developed after the main period of enrichment.[3] At Ray also, ac-

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 206, 1905.

[2] Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, p. 238, 1904.

[3] Ransome, F. L., this bulletin, p. 215.

cording to Ransome,[1] the layer of disseminated chalcocite ore has many irregular undulations that apparently have no dependence on the present topography.

It is not at all unlikely that secondary sulphide ores have formed independently of any present or past water level. As stated by Finch,[2] deposits exposed to processes of alteration in an arid region may lie in gaseous zones that are analogous to the aqueous zones of more humid regions. Oxygen predominates in the surface zone, whereas carbon dioxide and other heavier gases may prevail at greater depths. Thus in an arid region there may be an oxidizing gaseous zone and below it a reducing gaseous zone in which precipitation may take place in the absence of oxygen. Circulation by evaporation would be possible in the lower zone.

Precipitation by evaporation is undoubtedly a factor to be considered in shallow oxidizing zones and may account for the veinlets of clayey limonite that are found in cracks in some sulphide ores at depths considerably below the zones of nearly complete or well-advanced oxidation. The material precipitated by the evaporation of the mineral waters should be chemically similar to that deposited by evaporation under surface conditions, and, so far as analyses show, mineral waters that accomplish sulphide enrichment generally carry iron, aluminum, and other metals of low value greatly in excess of the more valuable metals. Unless, by processes of selective precipitation, certain compounds only could be removed from the solutions in depth, nearly all of the material dissolved in the oxidizing environment and carried below into the reducing environment would be precipitated. There would be a downward circulation of water and dissolved mineral matter. The upward circulation of evaporated water might carry some of the dissolved salts, but few data are available on this point. Weed states that ferrous, copper, and zinc sulphates are carried by the moisture of air circulating in mine openings. He thus accounts for efflorescence of these salts on mine workings.[3] Since mineral matter could not readily escape, however, the enrichment that could take place where downward-moving aqueous solutions could not reissue would depend on the sum total of the openings available, for appreciable replacement under these conditions would probably not occur. The secondary materials that are deposited under such conditions as a whole would not be much if any richer than the residues of descending waters, although even under these conditions the valuable minerals might be segregated somewhat by selective precipitation.

[1] Ransome, F. L., this bulletin, p. 216.

[2] Finch, J. W., The circulation of underground aqueous solutions and the disposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, p. 240, 1904.

[3] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 99, 1912.

THE PRIMARY ORE.

Since the primary ore extends downward generally to indefinite and almost always to unknown depths, the primary ore body can seldom be properly designated as a "zone." Yet, as has already been stated, many primary ore bodies that are workable near the surface become poorer in depth. At some places also, as in some deposits in the Bisbee district, Arizona, and at Georgetown, Colo., the primary ores have been enriched to the bottoms of the original primary ore shoots.

It may be repeated here that many ore bodies that have not been enriched by superficial processes are workable in the primary concentration; indeed some of the largest deposits in the world show little evidence of such enrichment.

The term "primary ore" is commonly used to designate valueless material that on weathering becomes an ore through superficial enrichment. Obviously, since the material is not workable, it is not strictly speaking an "ore." For such material Ransome[1] has proposed the convenient term *protore* to designate the "valueless material which generally underlies ores formed by sulphide enrichment and which would be converted into ore were the enriching process continued to sufficient depth." In this paper, with Mr. Ransome's consent, this term is used to designate the unchanged portion of any primary material that locally has been concentrated into ore, and that which by weathering may be so concentrated. Thus the low-grade porphyry beneath the disseminated copper ores of Bingham, Utah, of Ely, Nev., and of Santa Rita, N. Mex., may be termed "protore"; likewise the greenalite and cherty iron carbonate rocks of the Lake Superior iron ranges and the parent rock below the residual iron ores of Cuba are so designated.

PRECIPITATION OF METALS OUTSIDE OF PRIMARY ORE BODIES.

Metals in deposits undergoing weathering may not all be reconcentrated and preserved as a result of secondary enrichment.[2] Some may be carried away in the run-off, mechanically or in solution; some may be redeposited in the wall rock, making a deposit of a grade higher or lower than that of the original ore. The amount of scattering of the metals depends upon the structural features which determine the shape and attitude of the deposit and the nature and extent of fractures that involve the deposit. Physiographic conditions and the position of the water level also are important.

The scattering of the metals dissolved is most marked in the oxidized zone, where the ground is generally more open, but it may take

[1] Ransome, F. L., Discussion: Econ. Geology, vol. 8, p. 721, 1913.

[2] Penrose, R. A. F., jr., Certain phases of superficial diffusion in ore deposits: Econ. Geology, vol. 9, pp. 20–24, 1914.

place also around the zone of secondary sulphide deposition. Adequate treatment of the subject must include a review of the chemical relations of the metals involved and the rate at which they react on minerals in the wall rock when the metals are redeposited. Many deposits indicate loss. The weathering of the copper deposits of Ducktown, Tenn. (p. 236), during the period of base-leveling—that is, before the last period of rejuvenation—was probably attended by great loss, and doubtless the material dissolved from the ores was carried away in the run-off. At the Reforma mine,[1] Mexico, the tight condition of the copper lode has prevented deep oxidation, and weathering is attended by reprecipitation of little or no copper. Copper sulphide is readily dissolved and in the oxidized zone copper is mobile. Copper is readily precipitated as compounds stable in the absence of air, and its migration or scattering in the deeper zones is more restricted. At Butté, Mont., however, in the Anaconda vein, streaks of chalcocite run out many feet into the walls, apparently in granite that had no ore of the earlier period of mineralization.[2] The few known examples of this kind appear to be of relatively little importance compared with secondary ore bodies reprecipitated on older sulphides. In the oxidized zones of copper deposits where fractures lead away from the decomposing ore body and into the country rock there may be seats of mineralization on a larger scale. Valuable ore bodies are more likely to be reconcentrated where the country rock is limestone, because limestone causes precipitation of copper more rapidly than the other common rocks. Where the walls are feldspathic igneous rocks, scattering is likely to be more widespread and to result in loss.

Gold, in its deposits that are free from manganese, is likely to be concentrated at the outcrop and in placers near by. In manganiferous ore deposits there may be solution but probably not much loss by scattering, because gold is precipitated so readily and by so many agents. Nevertheless there is good evidence that small deposits of gold have formed in crevices where in all probability no gold deposits existed before. An example in Pinal County, Ariz., is cited by Tolman,[3] where "gold mirrors" with manganese are deposited in cracks in rhyolite. Probably of analogous origin are the "points" of the Mad Mule mine, Weaverville quadrangle, Cal., described by Ferguson, where gold, evidently derived from deposits near by, has been reprecipitated about small calcite lenses lying near a slate footwall. In calcite or other carbonate rocks, or in alkali-rich igneous

[1] Finch, J. W., A geological journey in Guerrero: Min. and Sci. Press, vol. 101, p. 498, 1910.

[2] Winchell, H. V., Discussion of paper by L. C. Graton and Joseph Murdoch on The sulphide ores of copper: Am. Inst. Min. Eng. Trans., vol. 45, p. 91, 1914.

[3] Tolman, C. F., Secondary sulphide enrichment: Min. and Sci. Press, vol. 106, p. 41, December, 1913.

rocks, such as some of those of Cripple Creek, one would not expect gold to travel far, because such rocks reduce gold solutions with great rapidity.[1]

In some deposits of silver, particularly in arid climates, the formation of the chloride restricts migration. In other deposits silver migrates readily. Where the silver travels outward in solution into the country rock it is precipitated less readily than gold or lead. At Leadville workable deposits have been found in porphyry near oxidizing bodies of silver-lead ore where no older ore body appears to have been present. (See p. 269.)

On oxidation deposits of zinc sulphide give zinc sulphate, a salt that is highly soluble in water. It reacts but slowly with most ore and gangue minerals and will therefore migrate farther before precipitating zinc. But in carbonate rocks or in calcite gangue the insoluble zinc carbonates are deposited, and around bodies that are undergoing oxidation in limestone valuable bodies of zinc carbonate ore may form. These are discussed on page 374.

Lead salts formed by oxidation have low solubilities, and under all conditions of superficial alteration lead appears to be nearly immobile. Some examples of scattering of several other metals are mentioned in sections of this paper where the metals are treated separately.

ESTIMATES OF VERTICAL EXTENT OF PORTIONS OF LODES ERODED.

Where there is reason to suppose that the primary ore was of approximately uniform composition before secondary alteration took place, it is possible to estimate the vertical extent of the portion of the deposit that has been eroded. As already stated, the ore in the secondary zone generally contains the valuable metals that were present in the primary ore, those that were leached from the oxidized zone above the secondary sulphide ore, and those that were leached from the portion of the deposit that has been removed—the metals that were carried downward by solutions in advance of erosion.

Estimates made for the Granite-Bimetallic lode, Philipsburg, Mont., indicate that at least 1,600 feet of material like the primary ore in the bottom of the mine was required to supply the valuable minerals in the secondary sulphide zone, in addition to those of the primary ore and any that may have been dissolved from the oxidized zone and reprecipitated below. Estimates for Ducktown, Tenn., on the other hand, show that the valuable minerals in the secondary sulphide zone may be fully accounted for by the reconcentration of

[1] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 748, 1914.

copper formerly in the leached zone now exposed, and that the copper that was present in the part of the lodes removed by erosion was scattered, probably while the region was at base-level.

The vertical extent in feet (x) of the part of the lode that has been removed from above the present apex of the deposit may be computed by the following equation, in which a equals the vertical extent in feet of the leached zone, b the vertical extent in feet of the enriched zone, l the assay content per ton remaining in the leached zone, e the similar content in the enriched zone, and p the similar content in the primary ore:

$$x=\frac{a(l-p)+b(e-p)}{p}$$

This formula does not take into account the changes in mass in the ore itself nor the pore space formed, but if value can be expressed as assay contents per unit of volume, changes in mass are accounted for. It is recognized, of course, that many other factors may modify the results; for the metal content may not all be reconcentrated, and the primary ore body, before alteration and enrichment, may not have been of equal size and richness throughout the deposit. The estimates therefore give only a rude approximation, but one which may be used, in connection with other geologic data, as a check on conclusions regarding the minimum amount of erosion that has taken place since the primary ore was deposited.

TEXTURES OF SECONDARY ORES.

OPEN SPACES.

In the zone of oxidation solution ordinarily much exceeds precipitation. The oxidized ore is generally of spongy open texture and contains numerous solution cavities. The iron ores formed by the weathering of ferruginous igneous or sedimentary rocks are almost invariably open textured, although in some the pore space formed by removal of valueless material is eliminated or closed by slumping near the surface and in some deposits by cementation with iron oxide at lower depths. Gossans of sulphide ores contain many openings ranging in size from minute pores to enormous caves. In such openings stalactites, stalagmites, organ pipes, iron straws, botryoidal masses, and reniform bodies are characteristic. These are formed principally of limonite, subordinately of carbonates and other compounds. Stalactitic, botryoidal, and similar forms are practically unknown in primary lode ores. In the secondary sulphide zone solution does not exceed precipitation to the same extent.

In the sulphide zone solution cavities may be developed, but these are likely to be filled, partly or completely, by secondary minerals. Yet the texture of secondary sulphide ore varies widely. Some of the chalcocite ore of Ducktown, Tenn., is little more than a sponge of chalcocite from which iron, copper, and other sulphates have been dissolved. On the other hand, some secondary sulphide ores consist largely of massive chalcocite inclosing numerous primary minerals, the pore space in the ores being quite subordinate.

Chalcocite, argentite, and other dark silver and copper minerals are frequently found as sooty amorphous powder coating firmer and more distinctly crystallized minerals. In Mexico and South America the dark ore containing these minerals is called negros or negrillos, contrasting with the red or yellow gossan ores above, called colorados, and the yellow or lighter colored ore below. Commonly, but not invariably, the sooty sulphide ores are secondary. Under some conditions the primary sulphides break down and form dark powdery material in an early stage of oxidation.

Many fractures formed by movement in primary ore are filled by secondary minerals. These have already been discussed (p. 38).

NEGATIVE PSEUDOMORPHS.

In ores from which certain minerals have been dissolved and in which other minerals remain intact the empty spaces may be bounded by surfaces that represent former surfaces of dissolved crystals. These spaces are commonly developed in the gossan of quartz-pyrite deposits, particularly where quartz predominates, the quartz locally surrounding the crystals of pyrite. Galena, tungstates, and many other minerals in quartz will likewise be dissolved and leave their negative pseudomorphs. Of nearly related genesis is the texture shown by imbricating blades of quartz which join at angles that represent the cleavage of calcite. Ore of this character is found in the oxidizing zone of deposits at Bullfrog and Manhattan, Nev.; at De Lamar, Idaho; Marysville, Mont.; and in many other calcitic deposits. If the undissolved calcite from below such ore is examined in thin section the genesis of these structures becomes obvious. The cleavage cracks of the calcite are filled with numerous thin plates of quartz, and after calcite has been removed the quartz plates remain and preserve the cleavage of the calcite. If the carbonate carries manganese, as it commonly does, the quartz septa are heavily stained with black or chocolate-colored manganese oxide. Material containing solution cavities may itself be wholly primary, but as the minerals removed are dissolved more readily in the oxidizing zone the negative pseudomorphs generally suggest superficial alteration.

NODULAR AND OOLITIC TEXTURES.

Oolitic rocks are those with textures resembling fish roe. In pisolitic rocks the spheres are as large as peas, and in nodular rocks they are commonly larger, some of them much larger. Nodular is applied, however, to spheres of all sizes. Oolitic, pisolitic, and nodular textures are found under widely different conditions. Marine ferruginous beds of oxides, carbonates, and silicates of iron are commonly oolitic. Weathered iron-bearing rocks and weathered aluminous rocks are commonly oolitic or pisolitic.

Rothpletz[1] states that calcareous oolites on the shores of Great Salt Lake and on the shores of other lakes and seas are due to action of algæ. Siliceous oolites are extensively developed in limestone in Cambrian and Ordovician strata in central Pennsylvania. Moore[2] regards these as replacements of the limestone. Hovey[3] regards the oolites as deposits formed by deposition about nuclei of sand of material from hot springs. Ziegler[4] concludes that some of the oolitic layers are replacements of oolitic limestones, but that most of them are due to direct deposition of silica from solutions, probably hot, about pure quartz sand. This replacement occurred, he assumes, on seashores in Carboniferous time, for angular fragments of normal limestone are inclosed in siliceous oolites. E. F. Burchard[5] has shown that Clinton iron ore oolites are commonly formed about sand grains.

At Saratoga, Tex., oolitic barite, according to Moore,[6] has been deposited 1,000 feet below the surface by ascending thermal waters. That oolitic texture may form also in cold nonmarine waters is indicated by its development by ordinary weathering as noted above. A lime carbonate mud, formed by precipitation from mine waters in the 2,000-foot level of the Geyser mine, Custer County, Colo., is oolitic.[7]

Primary sulphide lode ores rarely show oolitic structure, though such structure appears perhaps in some ores that were formed almost at the surface, where conditions were probably like those at the orifices of hot springs. In the Bassick mine, Custer County, Colo.,[8] nodules with banded crusts are formed about rounded rock frag-

[1] Rothpletz, August, On the formation of oolite: Translation in Am. Geologist, vol. 10, p. 279, 1892.

[2] Moore, E. S., British Assoc. Adv. Sci. Rept. 1911, p. 390, 1912.

[3] Hovey, E. O., Geol. Soc. America Bull., vol. 5, p. 627.

[4] Ziegler, Victor, The siliceous oolites of central Pennsylvania: Am. Jour. Sci., 4th ser., vol. 34, p. 127, 1912.

[5] Burchard, E. F., The red iron ores of eastern Tennessee: Tennessee Geol. Survey Bull. 16, p. 74, 1913.

[6] Moore, E. S., Oolitic and pisolitic barite from the Saratoga oil field, Texas: Geol. Soc. America Bull., vol. 25, p. 77, 1914.

[7] Emmons, S. F., The mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 459, 1896.

[8] Idem, p. 432.

ments by primary processes, but such deposits are very rare, and are probably due to unusual conditions. The pitchblende ores of Annaberg, Saxony, form spherulitic masses, which Bastin[1] considers primary. Superficial alteration, however, very commonly develops nodules of various sizes. The process in the oxidizing zone has been compared[2] to kernel roasting of copper-bearing iron sulphides, where iron oxide forms a shell about the grains and copper is concentrated toward their centers.

Such nodules may represent on a small scale the rearrangement of the metals with relation to depth. (See p. 57.) In the oxidation of iron-copper sulphides limonite forms outside, then copper oxide and sulphide between limonite and the original ore. In the oxidation of masses of silver-lead ores limonite and cerusite form outside, and the silver will be segregated with lead around galena.

Nodules form also in secondary sulphide zones. In some secondary deposits the small rounded cores of an older sulphide are coated over with shells of the secondary sulphide. As stated by Irving,[3] this in itself is evidence of replacement. That solution and precipitation went on simultaneously is indicated in such deposits by the even spacing of the cores. If solution had been completed before precipitation began, the small, rounded, partly dissolved masses would have settled and would have been massed closer. Of the chalcocite ore of the Old Dominion mine, at Globe, Ariz., Ransome[4] says:

> When the chalcocite is examined closely, particularly with a lens, it shows an indistinct unevenness of texture suggestive of the obscurer forms of pisolitic structure observed in some bauxites. Critical scrutiny of the inclosed grains of pyrite discovers the fact that their outlines are rounded and that the chalcocite has a more or less distinct concentric shelly structure around each grain. These facts at least strongly suggest that the chalcocite has been formed at the expense of the pyrite and that the minute structure observable in chalcocite now free from pyrite records the former presence of that mineral and its subsequent replacement by the sulphide of copper.

DEPOSITION IN CLEAVAGE CRACKS.

Secondary sulphides may be developed in cleavage cracks of pyrite, galena, and other minerals, and they may then show on polished surfaces a kind of indistinct network like the quartz in calcite mentioned above, the position of the thin blades being controlled by the cleavage of the older mineral.[5] In describing silver deposits of Gilpin

[1] Bastin, E. S., Geology of the pitchblende ores of Colorado: U. S. Geol. Survey Prof. Paper 90, p. 1, 1914.

[2] Read, T. T., The secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 37, p. 302, 1906. Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 56, 1910.

[3] Irving, J. D., Replacement ore bodies, in Bain, H. F., and others, Types of ore deposits, San Francisco, pp. 289–290, 1911.

[4] Ransome, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, p. 11, 1903.

[5] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 38, 1914.

County and Neihart, Mont., Bastin[1] notes that crystals of galena are replaced by polybasite along cleavage cracks. At both places the polybasite is believed to be deposited by downward-moving solutions.

Here also should be mentioned cleavage of chalcocite "inherited" from minerals it replaces. Graton and Murdoch[2] describe a specimen from the Copper Queen mine, Bisbee, where chalcocite replacing bornite shows a continuation of the cleavage lines of the latter. A similar structure is exhibited in ores of the Leonard mine at Butte. According to Ray[3] many ores at Butte retain ancient structures.

PSEUDOMORPHOUS REPLACEMENTS.

At depths below the earth's surface, particularly below the water level, the solution of primary sulphides and the precipitation of secondary sulphides may go on simultaneously along contacts and on outer surfaces, along cleavage planes, and in fractures that cut the older mineral. Thus the secondary mineral may replace the primary one. Becker[4] says: "The theory of the substitution of ore for rock is to be accepted only when there is definite evidence of pseudomorphic molecular replacement." In the earlier discussion of metasomatism, the term pseudomorphic replacement was used in this safe yet somewhat narrow sense to define a mineral substance that has the form of another mineral, particularly a crystal form that is not its own, or minerals that replace shells, plants, or other organic remains. More recently the criteria of metasomatic replacement has been extended, and many deposits that do not show crystal forms are assumed to have replaced other deposits. Such evidence, though less certain, is nevertheless suggestive, and used with other criteria it has greatly aided investigation. Pseudomorphs of chalcocite or covellite after pyrite, chalcopyrite, or zinc blende are the most common. Such replacements of pyrite are clearly shown in the Miami-Inspiration ore zone at Miami, Ariz.,[5] and at other places. Examples scarcely less suggestive are found in districts where masses of primary sulphide not having crystal form but of distinctive occurrence have been replaced by secondary ores. In the No. 20 mine near Ducktown, Tenn., where the primary ore, consisting chiefly of massive pyrrhotite, pyrite, and chalcopyrite, includes small rounded masses of quartz, garnet, and actinolite, the secondary ore consists of chalcocite and other minerals and includes similar rounded

[1] Bastin, E. S., Metasomatism in downward sulphide enrichment: Econ. Geology, vol. 8, p. 60, 1913.

[2] Graton, L. C., and Murdoch, Joseph, op. cit., p. 58.

[3] Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, p. 463, 1914.

[4] Becker, G. F., in Pošepný, Franz, The genesis of ore deposits: Am. Inst. Min. Eng. Trans., vol. 1, p. 205, 1888.

[5] Ransome, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 214, 1910.

masses of gangue minerals partly dissolved. At Morenci, Cananea, Bingham, Ely, Santa Rita, and in other districts containing disseminated deposits of secondary chalcocite, where the mineralized material below the secondary zone consists of a granular or a porphyritic igneous rock containing numerous small masses and veinlets of sulphide ore, chiefly pyrite and chalcopyrite, the same rock in the secondary zone contains small masses and veinlets of chalcocite, with some pyrite and chalcopyrite, showing an arrangement of spacing similar to that shown by the minerals in the lower zone. (See figs. 2 and 3.) Such evidence of replacement is scarcely less convincing than pseudomorphs having the regular boundaries of older crystals.

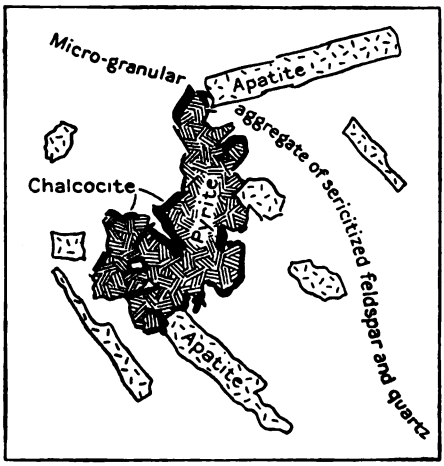


FIGURE 2.—Chalcocitization of pyrite. After Sidney Paige.

Some secondary chalcocite veinlets show narrow dark lines along their centers, which Graton and Murdoch[1] consider to represent the original fractures from which the veinlets have expanded. This feature was noted in ore from the Three R mine, Patagonia, and from Virgilina, Va., and Ajo, Ariz. The chalcocite of the original channel appears to be softer than that formed by replacement and more easily torn out by grinding.

Under the microscope some ores show, near the contact of two minerals, small particles of one inclosed in the other, the particles being much more abundant near the contact. This suggests that the inclosed mineral has been partly replaced by the inclosing mineral, but this criterion should be used with caution and in connection with other criteria, for it is obviously possible that such an ore may form by normal primary metallization. If the inclosed fragments are thinly spaced, and if all are oriented the same way and are oriented like the same mineral

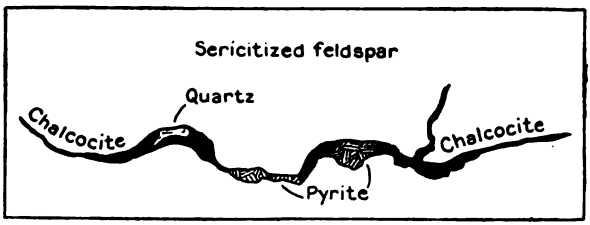
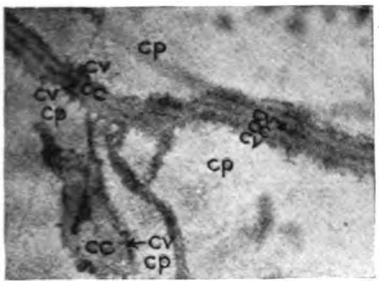


FIGURE 3.—Veinlet in sericitized feldspar filled with chalcocite, pyrite, and quartz. After Sidney Paige.

[1] Graton, L. C., and Murdoch,, Joseph, op. cit., p. 76.



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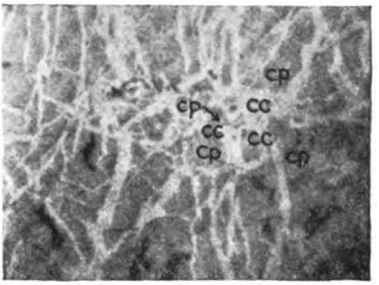

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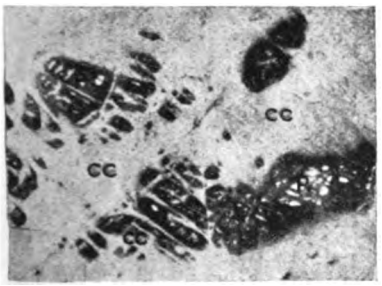

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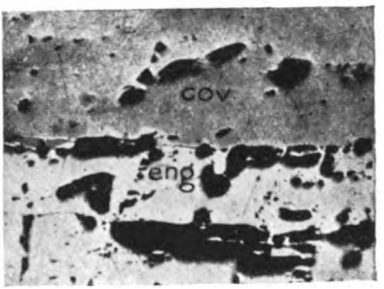

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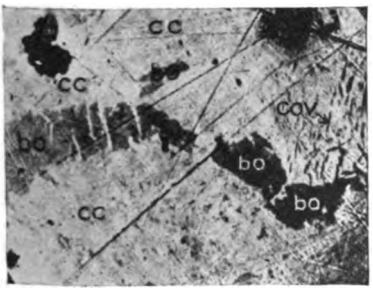

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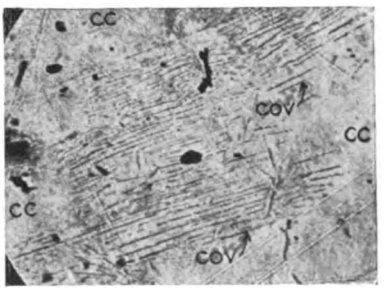


F

POLISHED SURFACES OF COPPER ORES.

A. Chalcopyrite (cp) cut by veinlets composed of covellite (cv) and chalcocite (cc), from Pilares mine, Nacozari, Sonora, Mexico. After Graton and Murdoch.

B. Chalcopyrite (cp) altering to chalcocite (cc), from Calumet & Arizona mine, Bisbee, Ariz. After Graton and Murdoch.

C. Strongly fractured and sheeted pyrite (p), largely converted into secondary chalcocite (cc), from Detroit mine, Morenci, Ariz. After Graton and Murdoch.

D. Covellite (cov) replacing enargite (eng), from 1,600-foot level of Leonard mine, Butte, Mont. After J. C. Ray.

E. Bornite (bo) and needles of covellite (cov) inclosed in chalcocite (cc), from 1,600-foot level of Leonard mine, Butte, Mont. After J. C. Ray.

F. Chalcocite (cc) replacing covellite (cov), from 1,600-foot level of Leonard mine, Butte, Mont. The area containing the minute needles of covellite is believed to represent a mass of covellite almost completely replaced by chalcocite. After J. C. Ray.

beyond the contact, the evidence of replacement is much stronger; but if the fragments are thickly spaced they may all be one crystal formed simultaneously and also simultaneously with the other mineral, as quartz and feldspar form in graphic granite. The significance of oolitic and nodular textures is discussed above. Secondary ores are shown in Plate I.

CEMENTATION TEXTURES.

Much of the material which is generally termed secondary sulphide ore consists essentially of shattered and fractured primary sulphide ore, the cracks in which are filled with later sulphides, or of angular fragments of the earlier sulphides crusted over with those that were introduced later. Primary ore fractured and enriched is illustrated by figure 4. Such textures, however, do not invariably indicate processes of sulphide enrichment by descending solutions. Many authentic examples show that, in the course of primary mineralization, the ore first deposited has been fractured and that solutions from below have deposited later sulphides in the fractures. The ore illustrated by figure 5 may be all primary. In many deposits the later sulphides are richer than the original fractured ore.

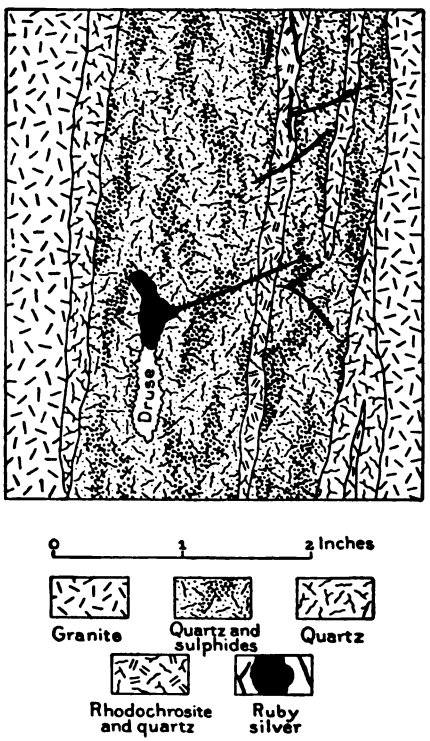


FIGURE 4.—Banded ore from south vein, Granite-Bimetallic lode, Philipsburg, Mont., showing secondary ruby silver in vugs and cracks. After W. H. Emmons and F. C. Calkins.

Pseudomorphous replacement indicates a change of physical conditions or of chemical environment. Minerals that were stable under certain conditions have been dissolved and other minerals have simultaneously been deposited. On the other hand, fractured ore cemented by later minerals may be a result of normal and perhaps continued deposition from below. If, however, the minerals that fill the later cracks are those that are commonly formed by descending solutions, and if they do not persist in depth, the assumption that they are secondary may with considerable confidence be regarded as confirmed.

In many deposits the genesis of such later veinlets is perplexing. As the matter now stands, the mineralogic criteria are unsatisfactory, for few if any of the sulphides are formed invariably under a single set of conditions.

The texture of the secondary veinlets is important, however, and it may throw considerable light on their genesis. Concerning this point certain observations by Hynes[1] on ores from the Mina Mexico vein, Sonora, Mexico, are noteworthy. The polished surfaces of several specimens prepared by him showed primary ore composed of pyrite and quartz not containing any antimony mineral, cut by veinlets of ore composed of tetrahedrite and quartz. In the later veinlets the quartz is everywhere inclosed in the tetrahedrite and is generally idiomorphic. Its crystals are distributed with great regularity through the tetrahedrite, suggesting definite or "eutectic" proportions.

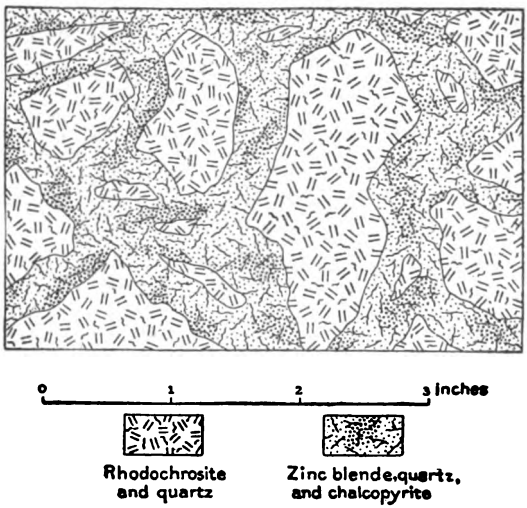


FIGURE 5.—Ore from Granite vein, level 8, Philipsburg, Mont. Fragments of rhodochrosite and quartz are cemented by an ore composed of zinc blende, quartz, and chalcopyrite. Both generations may be primary. After W. H. Emmons and F. C. Calkins.

When in the course of the deposition of ores the minerals are deposited layer on layer in open spaces, the minerals forming the last layer or crust may differ from those formed earlier, and when cavities are broken open the minerals last deposited appear to be of late age. The position of the mineral lining the cavity does not certainly indicate that it was deposited by descending waters, for the last ores deposited by ascending waters in open spaces would be in a similar position. Crustified banding, though much less common in secondary than in primary ores, is not unknown in them. If, however, the walls of cavities and fractures are coated with the hydrous oxides of iron or manganese, and if sulphides have formed along with these oxides, there is small probability of error in determining whether the sulphides were formed by ascending or descend-

[1] Hynes, D. P., Notes on the geology of the Mina Mexico vein: Econ. Geology, vol. 7, pp. 280–286, 1912. See also Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 76 (fig. 13, showing chalcocite inclosing idiomorphic crystals of quartz and pyrite), 1912.

ing solutions, for the hydrous oxides are rarely deposited with primary sulphide ores. Likewise the intimate association of native metals with such hydrous oxides is generally evidence of deposition by oxidized descending solutions.

GRAPHIC INTERGROWTHS.

Peculiar intergrowths of chalcocite and bornite occur in ores of the Virgilina district, Virginia,[1] of the Mount Lyell mine, Tasmania,[2] at the Engels mines, Plumas County, Cal.,[3] and of the Bevelheymer mine, near Reno, Nev.[4] These are frequently termed "graphic intergrowths," because they resemble in general appearance the intergrowth of quartz and feldspar in graphic granites. The appearance of these structures (see Pl. II) Ransome[5] has aptly termed "ordered irregularity." The sharp angles and sharp contacts suggest that of the two minerals each has influenced the crystallization of the other, which leads to the inference that they were formed at the same time and not that one mineral replaced the other along cleavage cracks. Moreover there is fairly even spacing, suggesting that the ore was deposited by a solution of uniform composition, possibly one with the metals in "eutectic" proportions. It is believed by some that these sharp graphic patterns are not developed by secondary processes; certainly they are not developed by such processes near the surface, where iron and copper strongly tend to segregate.

SUBGRAPHIC PATTERNS.

A specimen of chalcocite and bornite from Butte shows an intergrowth less well ordered,[6] and one from Bisbee[7] shows chalcopyrite and bornite with a similar intergrowth. Graton and Murdoch term such a structure "subgraphic" and consider it to indicate primary metallization. Ransome[8] found bornite and chalcopyrite similarly intergrown in the Queen mine, near Superior, Ariz., where there is considerable evidence that most of the bornite is secondary. (See

[1] Laney, F. R., The relation of bornite and chalcocite in the copper ores of the Virgilina district of North Carolina and Virginia: Econ. Geology, vol. 6, pp. 399–411, 1911. Especially Pl. VII, fig. 2.

[2] Gilbert, C. G., and Pogue, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., vol. 45, p. 618, 1913.

[3] Rogers, A. F., Secondary sulphide enrichment of copper ores, with special reference to microscopic study: Min. and Sci. Press, vol. 109, p. 680, 1914.

[4] Segall, Julius, The origin and occurrence of certain crystallographic intergrowths: Econ. Geology, vol. 10, pp. 462–470, 1915.

[5] Ransome, F. L., Copper deposits near Superior, Ariz.: U. S. Geol. Survey Bull. 540, p. 148, 1912.

[6] Graton, L. C., and Murdoch, Joseph, op. cit., p. 76.

[7] Idem, p. 80.

[8] Ransome, F. L., op. cit., p. 149.

fig. 6.) A. F. Rogers[1] found such structures in chalcocite and bornite ore at the Engels mine, Plumas County, Cal., but he regards the

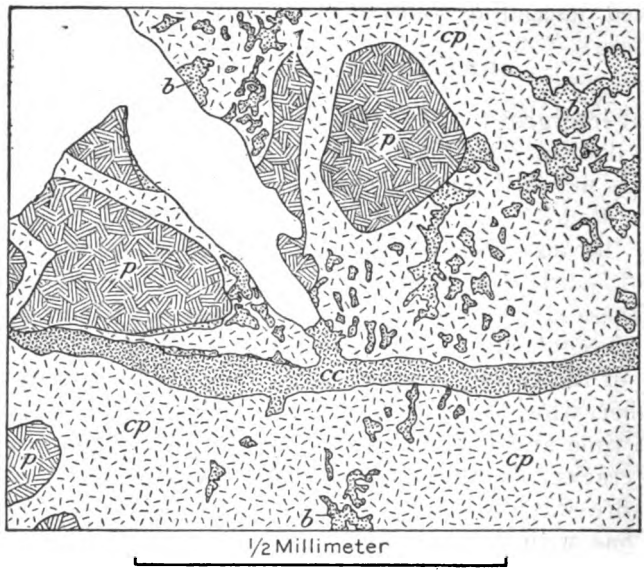


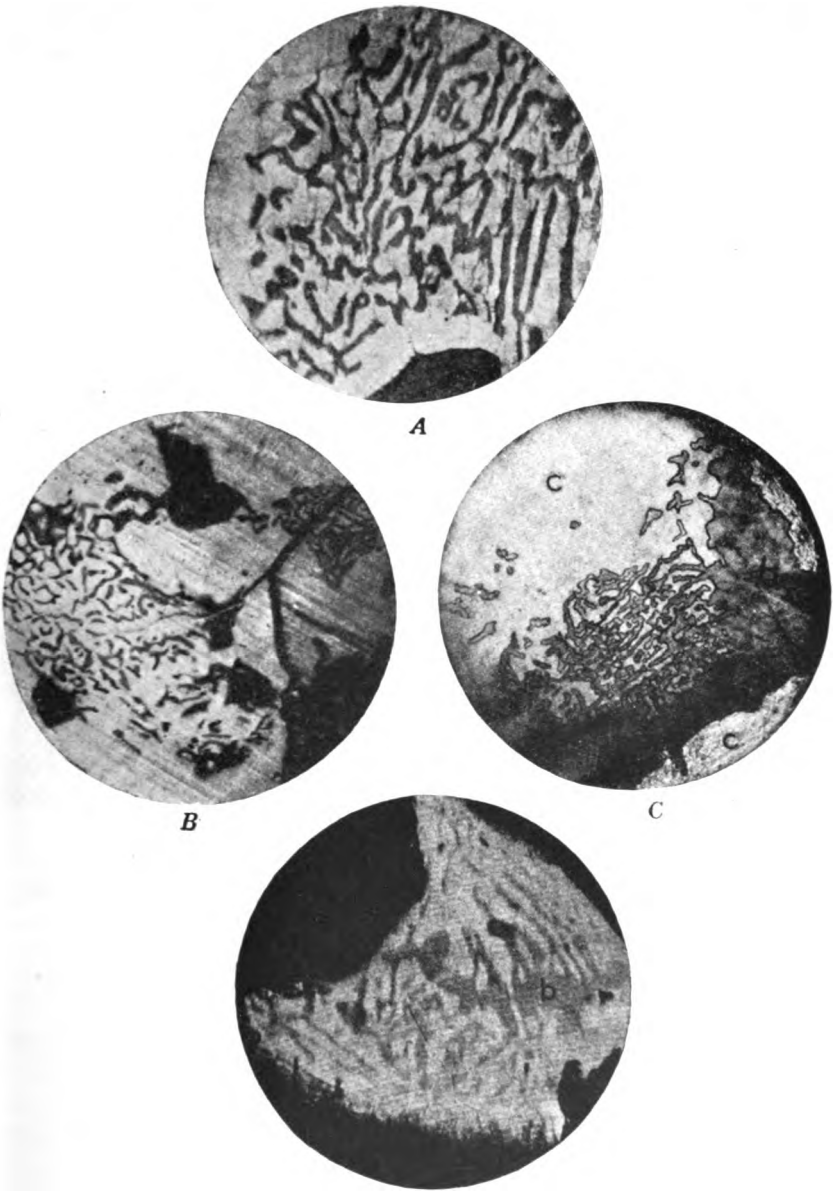
FIGURE 6.—Polished surface of ore from Queen mine, Superior, Ariz. Shows remnants of pyrite (*p*) surrounded by chalcopyrite (*cp*), with bornite (*b*) in areas suggestive of intergrowth with chalcopyrite. Chalcocite (*cc*) in a distinct veinlet. After F. L. Ransome.

chalcocite as a replacement developed in the bornite. It appears probable that ores showing "subgraphic" textures may be formed either by primary or secondary processes.

SUMMARY OF CRITERIA FOR IDENTIFICATION OF SECONDARY ORES.

Because many ores owe their workable grade to secondary processes it is important to note the features by which the results of secondary processes may be recognized. As secondary ores are superficial they will play out in depth, so that the problems of enrichment are vital to intelligent exploitation. A statement of all the principles involved would include much of the data presented in this paper, for metals behave differently, and a statement of the criteria for the determination of secondary ores must give proper weight to such differences. The migration of metals depends upon the ore and gangue and upon many other factors reviewed above; yet certain

[1] Rogers, A. F., Secondary enrichment of copper ores, with special reference to micrographic study: Min. and Sci. Press, vol. 109, p. 685, 1914. See also Segall, Julius, op. cit., p. 466.



POLISHED SURFACES OF GRAPHIC ORES OF BORNITE AND CHALCOCITE.

A. Intergrowth of chalcocite (light) and bornite (dark), from Wall mine, Virgilina district, Virginia. After F. B. Laney.

B. Intergrowth of chalcocite (light) and bornite (dark), from Bevelheymer mine, Washoe County, Nev. Courtesy of Mr. Julius Segall.

C. Intergrowth of chalcocite (c) and bornite (b), from Mount Lyell copper district, Tasmania. After Gilbert and Pogue.

D. Bornite (b) and chalcocite, from Engels mine, Plumas County, Cal. After A. F. Rogers.

general principles may be applied to the investigation of all deposits. These have been treated elsewhere but will be summarized briefly here.

Secondary ores may be divided into two classes—ores formed by the removal of valueless material and enriched by subtraction and reduction of mass, and ores enriched by precipitation or by substitution of metals.

Ores formed by the removal of valueless material without much addition of valuable material exhibit certain characteristic features. (*a*) They are porous, the pores representing the material that has been removed; slumping near the surface and cementation below operate to close pore spaces. (*b*) They generally grade downward into low-grade ore or protore. (*c*) They show an evident relation to the present or to a former surface and commonly but not always to the ground-water level; the deposits are likely to be thicker under a hilltop, where the outcrop is high and the water level is farther below the outcrop than in valleys. Ores of this character are commonly developed on base-leveled surfaces and are found on plateaus or in elevated regions, on such surfaces that have been raised since the ores were formed. Circulation may have been controlled by structural features, and the deposits, enriched by removal of valueless material, may be found in the more highly fractured masses, because circulation was more active there, or in structural basins or pitching troughs. (*d*) They have been concentrated at the surface because the metals they contain are not readily removed by solution; in many places they have been removed by mechanical erosion from the outcrops, and commonly they are found along streams or in beds that have been formed by mechanical disintegration and deposition near by. Placers of gold and tin and detrital iron oxide sediments are commonly formed near older deposits containing those metals or in overlying unconformable rocks, particularly in basal conglomerates. (*e*) Their minerals are those that are stable under surface conditions, the so-called "end products" of weathering—iron oxides, kaolin, bauxite, manganese oxides—and the stable residuals, such as magnetite and chromite, and in some deposits gold, cassiterite, and monazite.

Ores enriched by addition—that is, by precipitation or substitution of certain metals—also show certain characteristic features: (*a*) They may be porous and open textured, particularly in the oxidizing zone, though at greater depths cementation tends to close openings. (*b*) They commonly show characteristic changes downward, a leached zone at and near the surface grading into a zone of higher grade sulphide and this into a zone of primary ore. Although

these zones are developed in most of the deposits of this group they are not developed in all, and rapid erosion may remove the ore of one or all of the secondary zones. (*c*) The secondary zones of such ores will be related to the topography that existed when they were formed, their tops generally lying farther below the surface, yet at higher elevations below hilltops than below valleys. The top of the secondary sulphide zone is generally related also to the water level that existed when it was formed, but subsequent changes of the water level may obscure this relation, particularly in arid countries. Where the water level lies very deep some secondary sulphide ores appear to have formed above and independent of the water level. As stated elsewhere, many primary ores that are formed near the surface show a relation to the topography that existed when they were formed because the maximum precipitation of the metals in the original ore body was accomplished by the mingling of ascending hot waters with cold and perhaps oxidized meteoric waters, or by the escape of gases that had held the metals in solution, or by other processes. Thus a relation of the rich zone to the present topography is a more nearly certain criterion if applied to older and more deeply eroded deposits than to younger ones that may have formed under topographic conditions that were perhaps similar in essential features to the topography now existing. (*d*) The metals that are concentrated by transportation and precipitation are those that go into solution and consequently those that are commonly leached from outcrops. Thus a porous leached outcrop stained with iron will suggest secondary ores below, and a great many deposits are found by following downward nearly barren gossans. But erosion may be so rapid that the gossan is not completely leached, and the valuable metals may not all be removed. Thus placers may form from a deposit whose gossan is only partly leached; or by still more rapid erosion the gossan or even the secondary sulphide zone itself may be removed and the primary ore exposed at the outcrop. This criterion should be applied with great caution and with adequate understanding of the physiography and geology of the region. Otherwise it is likely to lead to error. Altered zones that have been tilted or faulted or covered with later igneous rocks or sedimentary beds are discussed elsewhere in this bulletin. (*e*) The groups of minerals of the several zones are characteristic. Few sulphide minerals are exclusively primary or exclusively secondary, yet some are essentially one or the other, and in nearly all deposits an adequate study of the minerals and their relations will throw much light on the genesis of the deposit. As the heavy silicates and several other minerals that are characteristic of deposits formed at considerable depths are not formed by secondary processes, the mineralogic criteria are more satisfactory when applied to these deposits. Chem-

ical and geologic data on mineral genesis are now accumulating very rapidly and promise to make such criteria more certain. The value of each common mineral as indicating genesis is discussed elsewhere in this paper. (*f*) The texture of an ore and its paragenesis is important and will frequently indicate its origin. The primary minerals are, by the definition of the terms, earlier than the secondary ones, which are formed in cracks cutting the earlier ore, or replace it along such cracks. The mere fact that one association of minerals is found in cracks in an older association of minerals, or that one mineral is a metasomatic replacement of another is not in itself an indication of its deposition by downward-moving waters. Many veins are fractured after they are formed, and ascending waters deposit minerals of different composition in them. Therefore this criterion may not lead to a final decision, but it should be used, proper weight being given to the mineral composition of the older and younger groups of minerals, to the relation of the ore body to other zones, and to other facts and conditions. (*g*) From the study of a large number of deposits we learn that certain downward changes may be considered standard. There are exceptions, it is true, but the reasons for them become more clear as information is accumulated. These standard changes, which are different for each of the metals and commonly for each metal in different mineral associations, are discussed later. (*h*) The vertical extent of a secondary sulphide zone, though depending somewhat on the topography, the duration of the period of erosion, geologic history, and environment, should nevertheless show a relation to the permeability of the primary ores and to their mineral composition. In permeable primary deposits the valuable metals may be carried farther before they are precipitated than in ores less permeable; but in equally permeable ores the rates at which the metals are precipitated varies greatly. The secondary sulphide zone will have smaller vertical range in deposits whose primary ores react readily to precipitate the metals. These relations for each important metal are discussed in the following pages. (*i*) Secondary ores will not contain elements not in the primary ores or in the country rock or in air or surface waters. The absence in the primary ore of at least small amounts of elements in supposed secondary minerals should lead to doubt as to the validity of the conclusion, unless such elements are present in the wall rock or in the air or surface waters.

CHEMISTRY OF ENRICHMENT.

GENERAL CHARACTER OF UNDERGROUND WATERS.

Underground waters are chiefly solutions of carbonates, chlorides, and sulphates of the alkalies, alkaline earths, and other metals. Some waters that were trapped in sediments when they were deposited are

ancient sea waters and are therefore rich in chloride. Broadly speaking, the hot waters in areas of recent volcanism are alkali chloride waters, and the hot waters in regions where there are no late igneous rocks contain predominantly the alkali earth carbonates.[1]

Seventy-five analyses of hot springs and 42 analyses of mine waters have been tabulated and, when necessary, reduced to parts per million and to uniform statements so that they may more readily be compared. The analyses of hot springs have been divided into two groups, one representing springs that issue from regions of late volcanic activity, and one representing springs that issue from regions of more remote volcanic activity.

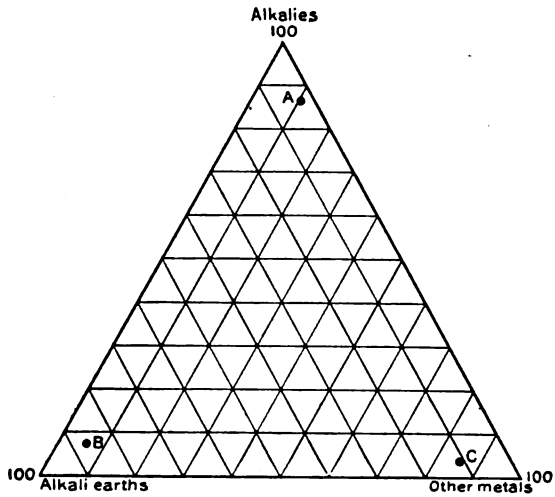


FIGURE 7.—Diagram showing relative proportions (reacting values) of alkalies, alkali earths, and other metals, in (*A*) an average of 58 analyses of hot springs from areas of relatively late volcanic activity, (*B*) an average of 17 analyses of hot springs from areas of remote volcanic activity, and (*C*) an average of 42 analyses of mine waters. After W. H. Emmons and G. L. Harrington.

A comparison of the averages of the results obtained shows that the waters of these three groups—the mine waters and the two groups of hot-spring waters—carry essentially the same elements, although they differ greatly in the amounts of the elements they carry. These differences are shown graphically by the triangular diagrams given above and on page 85. As shown by figure 7, the ascending hot waters in areas of relatively late volcanic activity (*A*) are essentially solutions of the alkalies, though they carry also alkaline earths and other metals. The hot waters in areas of remote volcanic activity (*B*) are essentially alkaline earth solutions, although they carry

[1] Emmons, W. H., and Harrington, G. L., A comparison of the waters of mines and of hot springs: Econ. Geology, vol. 8, pp. 653–669, 1913.

some alkalies and other metals. Mine waters associated with sulphide ores (*C*) are chiefly solutions of the heavy metals but contain appreciable amounts of alkaline earths and some alkalies.

In figure 8 the negative radicles, except those in group *A*, are likewise grouped in the corners of a triangular diagram. In the hot waters of regions of late volcanic activity (*A*) chlorides predominate, though there is but a slightly lower proportion of carbonates and also an appreciable proportion of sulphates. Hot waters in areas of remote volcanic activity (*B*) are essentially carbonate solutions, although they contain also sulphates and chloride in appre-

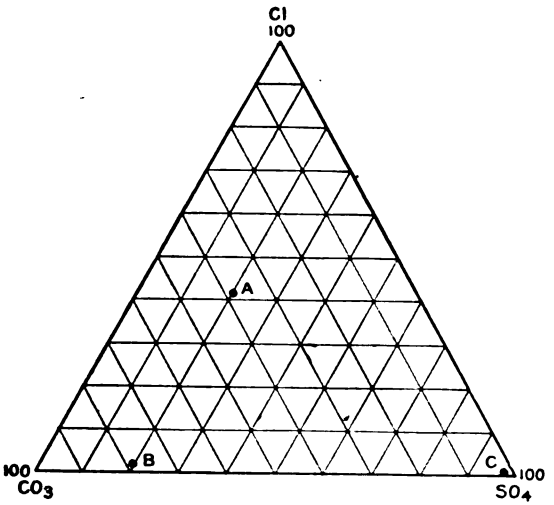


FIGURE 8.—Diagram showing relative proportions (reacting values) of Cl, CO_3, and SO_4 in (*A*) an average of 58 analyses of hot springs from areas of relatively late volcanic activity, (*B*) an average of 17 analyses of hot springs in areas of remote volcanic activity, and (*C*) an average of 42 mine waters. After W. H. Emmons and G. L. Harrington.

ciable quantities. Mine waters (*C*) are chiefly sulphate waters and carry only a little of the carbonates and chlorides.

Of the 42 analyses of mine waters, 41 are given in the tables on pages 87–89.

Hodge[1] has recalculated 50 analyses of waters in mines of sulphide ores to the system proposed by Palmer.[2] As indicated in figure 9, there is a remarkable uniformity in the character of these waters. Nearly all of them are essentially sulphates of metals with some alkalies and alkali earths, but they differ greatly as to acidity and state of oxidation. Calculated by the method proposed by Palmer,

[1] Hodge, E. T., The composition of waters in mines of sulphide ores: Econ. Geology, vol. 10, p. 123, 1915.

[2] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, p. 13, 1911.

22 are acid, 14 are neutral, and 14 are alkaline. These results, however, do not all agree with the determinations of acidity and alkalinity stated by the analysts, but they are the closest approximations that can be made with the methods employed. In some of the analyses carbon dioxide is obviously present, although it is not reported. With depth solutions change from acid to neutral and later become alkaline. According to Hodge, the average total concentration of salts per liter in acid waters is 2.96 grams, in neutral waters 0.82 gram, in alkaline waters 0.66 gram. All the positive radicals decrease with decreasing acidity, except the alkalies, which increase as acidity decreases. Silica decreases as the solution becomes neutral and increases with increase of alkalinity.

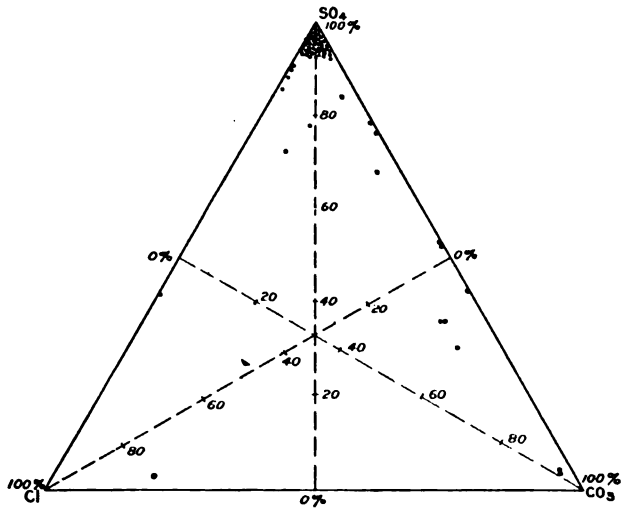


FIGURE 9.—Diagram showing relative abundance of SO_4, Cl, and CO_3 in 50 mine waters. After E. T. Hodge.

Even if carbon dioxide is added to analyses of neutral and alkaline solutions to balance all positive radicals, the concentration in acid waters is still much greater than in neutral and alkaline waters.

COMPOSITION OF WATERS IN COPPER AND PRECIOUS-METAL MINES OF SULPHIDE ORES.

ANALYSES.

The following tables show the results of analyses of 41 samples of water taken from mines containing deposits of sulphide ores:

Analyses of mine waters.

Waters of copper mines.

[Parts per million.]

	1	2	3	4	5	6	7	8
SO_4	406.5	544.7	90.6	593.4	71,053.3	2,672.0	6,664.0	2,068.0
Cl	6.8	118.5	11.8	842.8	17.7	13.0	.1	2.2
CO_3	13.2	Trace.						
PO_4	Trace.	Trace.	Trace.	Trace.	1.5	Trace.		
B_4O_7						Trace.		
Br						Trace.		
F						Trace.		
SiO_2	23.2	27.2	36.1	29.5	67.4	47.7	55.6	78.9
K	7.1	30.5	3.5	11.4	6.8	13.1	19.8	7.8
Na	16.2	176.9	11.1	82.8	41.7	39.6	23.4	5.9
Li	Trace.				Trace.			
Ca	151.2	92.7	49.0	512.1	307.7	132.5	67.6	238.0
Mg	28.2	17.9	10.3	102.6	149.2	61.6	40.6	63.3
Al	0.0				85.2	83.5	433.0	165.0
Mn	.5	Trace.	2.5	1.4	13.2	12.0	.2	.3
Ni					3.5	.5		
Co					4.6			
Cu	Trace.	.4			45,633.2	59.1	312.1	40.8
Zn	.3	1.8	1.9	0.0	411.2	852.0	199.8	54.3
Cd						41.1		
Fe''	1.8	1.4	.9	.4	49.8	159.8	2,178.0	1.3
Fe'''							0.0	186.3
Acidity: H_2SO_4	Alk.	Alk.	Alk.	Alk.			129.6	406.5

1. Green Mountain mine, Butte, Mont., 2,200-foot level in fissure in "granite," remote from known veins. Crosscut opened day before sample was taken. W. F. Hillebrand, analyst. Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 101, 1912.
2. Glengarry mine, Butte, Mont., 220-foot crosscut south. Very slightly alkaline. Black deposit containing FeS, much free sulphur, and probably ZnS. W. F. Hillebrand, analyst. Weed, idem.
3. Anaconda mine, Butte, Mont., 800 feet west. Very faintly alkaline; deposits iron and manganese. W. F. Hillebrand, analyst. Weed, idem.
4. Gagnon mine, Butte, Mont., 1,125 feet from shaft. Very faintly alkaline; deposits iron. Weed, idem.
5. Mountain View mine, Butte, Mont., second level. W. F. Hillebrand, analyst. Clarke, F. W., The data of geochemistry: U. S. Geol. Survey Bull. 616, p. 633, 1916; also Weed, op. cit.
6. St. Lawrence mine, Butte, Mont. W. F. Hillebrand, analyst. Clarke, op. cit.; also Weed, op. cit.
7. Burra Burra mine, Ducktown, Tenn., first level below black copper workings. R. C. Wells, analyst. Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.; U. S. Geol. Survey Bull. 470, pp. 171–172, 1911.
8. East Tennessee mine, Ducktown, Tenn., 30-fathom level. R. C. Wells, analyst. Emmons, W. H., and Laney, F. B., idem.

	9	10	11	12	13	14	15	16	17	18	19
SO_4	444.0	416.4	415.8	476.8	5,064	1,419	4,457	3,898	1,335	555.9	256.0
Cl	.7	.6	.7	.4	Undet.	18	22	Undet.		55.4	8.5
CO_3											153.4
PO_4											
B_4O_7											
Br											
F											
SiO_2	20.6	19.1	37.0	49.9	76	28	56	40	20	94.8	28.0
K	3.2	2.8	2.7	2.2	Undet.	[a]170	[a]198	[a]97	[a]14	27.9	11.0
Na	3.1	3.0	5.2	5.5						33.0	35.0
Li											
Ca	18.1	18.4	19.7	30.4	436	319	753	239	277	105.8	126.0
Mg	12.2	11.5	5.2	6.2	61	36	86	82	54	26.3	
Al	40.1	46.5	14.5	19.1	Undet.	16	22	44	9		
Mn	.3	.9	.2	.1	236	37	153	150	45		
Ni											
Co											
Cu	12.8	12.0	28.1	11.0	1,659		60	122	28		
Zn	6.1	4.2	2.4	2.9	Undet.	73	252	190	52		
Cd											
Fe''	Trace.	Trace.	71.4	89.2	305	76	524	799	149	36.4	19.0
Fe'''	29.9	31.3	20.3	55.9					24	42.0	0.0
Acidity: H_2SO_4	108.2	115.1	210.2	97.5	970	Nil.	Nil.	Nil.	Nil.		Alk.

[a] Calculated as K_2O+Na_2O.

9. No. 20 shaft (top), Ducktown, Tenn. Emmons and Laney, unpublished manuscript.
10. No. 20 shaft (bottom), Ducktown, Tenn. Emmons and Laney, idem.
11. Callaway shaft, Ducktown, Tenn., at water level. R. C. Wells, analyst. Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.: U. S. Geol. Survey Bull. 470, pp. 171–172, 1911.

12. Callaway shaft, Ducktown, Tenn., 37 feet below water level. R. C. Wells, analyst. Emmons, W. H., and Laney, F. B., idem.
13. Capote mine, Cananea, Mexico, 300-foot level. G. W. Hawley (chief chemist, Cananea Consolidated Copper Co.), analyst. Analyses 14 to 17 obtained through the courtesy of Mr. D. P. Hynes.
14. Capote mine, Cananea, Mexico, 400-foot level. G. W. Hawley, analyst.
15. Capote mine, Cananea, Mexico, 900-foot level. G. W. Hawley, analyst.
16. Capote mine, Cananea, Mexico, water pumped from mine. G. W. Hawley, analyst.
17. Capote, Puertacitas, Cananea-Duluth, and Democratic mines, Cananea, Mexico; water used at concentrator at Cananea. Circulates at concentrator in contact with ore and air. G. W. Hawley, analyst.
18. Ruth mine, Ely, Nev., bottom of inclined shaft. H. E. Miller, analyst. Lawson, A. C., The copper deposits of the Robinson mining district, Nevada: California Univ. Dept. Geology Bull., vol. 4, p. 332, 1906.
19. Brooks inclined shaft, Giroux Consolidated Mining Co., collected by A. C. Spencer, September, 1910. Chase Palmer, analyst. Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 645, 1913.

Waters of gold, silver, and gold and silver mines.

[Parts per million.]

	20	21	22	23	24	25	26	27	28	29
SO_4	43.20	161.70	380.38	474.00	209,100.00	173.40	272.30	160.00	7.70	7.80
Cl	7.90	186.40	1.27	19.00	127.60	.52	13.77	16.82	3.16	3.10
CO_3	110.50	1,513.44	115.03	20.45		47.71	241.39	194.70	141.80	146.60
NO_3		1.60								
PO_4	Trace.	Trace.								
S									1.10	
SiO_2	25.90	24.42	30.50	133.40	616.00	37.86	59.96	68.92	32.70	41.40
K	10.60	198.00	8.39	53.40		62.26	80.90	254.10	1.00	1.60
Na	36.40	719.45	57.13	132.00	535.00	.27	6.86	7.84	13.40	13.70
Li	Trace.	2.85								
Ca	37.40	146.41	148.10	100.10	1,286.00	72.37	113.70	84.08	33.60	44.35
Sr		1.95								
Mg	12.25	177.67	154.03	5.88	6,590.00				5.70	3.35
Al	.40	1.06		1.37	9,670.00					
Mn	.80	.57			885.10				.27	1.90
Ni										
Co										
Cu	Trace.	.02			147.50					
Zn	.20	.34								
Pb	Trace.	1.35							Trace.	Trace?
Fe''	.70	3.50				Trace.	Trace.	Trace.		
Fe'''				6.33	5,025.00	Trace.	Trace.	Trace.		
H (bicarbonates)									4.60	4.70
H (acids)					2,575.00				Alk.	Alk.
Fe_2O_3									4.20	1.80
Al_2O_3										
CO_2	37.29	1,418.61								

20. Geyser mine, Custer County, Colo., 500-foot level. W. F. Hillebrand, analyst. Emmons, S. F., The mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 461, 1896.
21. Geyser mine, Custer County, Colo., 2,000-foot level. W. F. Hillebrand, analyst. Emmons, S. F., idem, p. 462.
22. Savage mine (Comstock lode), Storey County, Nev., 600-foot level.
23. C. & C. shaft (Comstock lode), Storey County, Nev., 2,250-foot level. N. E. Wilson, analyst. Reid, J. A., The structure and genesis of the Comstock lode: California Univ. Dept. Geology Bull., vol. 4, p. 189, 1906.
24. Central tunnel (Comstock lode), Storey County, Nev., vadose water. N. E. Wilson, analyst. Reid, J. A., idem, p. 192.
25. Gould & Curry mine (Comstock lode), Storey County, Nev., 1,700-foot level.
26. Hale & Norcross tunnel section (Comstock lode), Storey County, Nev.
27. Gould & Curry mine (Comstock lode), Storey County, Nev., 1,800-foot level.
28. Federal Loan mine, Nevada City, Cal., 400-foot level. W. F. Hillebrand, analyst. Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 121, 1896.
29. Black Prince mine, Nevada City, Cal., 400-foot level. W. F. Hillebrand, analyst. Lindgren, Waldemar, idem.

Waters of gold, silver, and gold and silver mines—Continued.

[Parts per million.]

	30	31	32	33	34	35	36	37	38	39	40	41
SO_4	258.40	26.55	280.10	124.80	60.12	104.4	2,039.51	327.2	67.2	255.9	283.4	Trace.
Cl	Trace.	Trace.	Trace.	12.40	Trace.	1.6	8.16	35.6	15	Trace.	Trace.	16.8
CO_3					78.3	92.4		37.9	130	134.4	187.8	
NO_3								Trace.				
PO_4												
S												
SiO_2	2.10	8.00	8.80	18.00	32.25	23.2	43.80	64.8	55.3			
K					2.41	3.5	70	3.4	5.0			
Na					28.52	7.5	106.27	148.3	30.1			
Li												
Ca	90.76	72.48	106.20	46.40	17.36	46.2	187.15	68.8	39.1	136.3	123.3	2.8
Sr												
Mg	13.08	14.90	17.14	14.50	1.30	7.3	93.50	6.3	6.7	9.3	17.5	
Al	1.49	.37	1.49				3.12			(?)	(?)	(?)
Mn	4.74	4.12	1.88		.25	3.2	155.58	.7	.8	Trace.		
Ni	Trace.	Trace.	Trace.									
Co	Trace.	Trace.	Trace.									
Cu							77.05					
Zn	2.82	47.40	18.88	8.90			49.66	Trace.				
Pb							3.44					
Fe″				6.60	1.47	.85	164.82		.4	(?)	(?)	2.2
Fe‴	4.74	6.30	4.69					.7				
H (bicarbonates)										2.2		
H (acids)					Alk.	Alk.				Neutral	Neutral	Alk.
Fe_2O_3										1.2	0.8	
Al_2O_3												
CO_2					61.53	72.60				(?)	(?)	25.2

30-33. Rothschönberger Stolln, Freiberg, Germany. A. Frenzel, analyst. Beck, Richard, The nature of ore deposits (translated by W. H. Weed), vol. 2, p. 377, 1905.

34. Bachelor mine, Creede, Colo. Iron includes some aluminum. Water is alkaline. Chase Palmer, analyst.

35. Solomon mine, Creede, Colo. Iron includes some aluminum. Water is alkaline. Chase Palmer, analyst.

36. Stanley mine, Idaho Springs, Colo. L. J. W. Jones, analyst. Jones, L. J. W., Ferric sulphate in mine waters and its action on metals: Colorado Sci. Soc. Proc., vol. 6, p. 48, 1897-1900.

37. Mizpah mine, Tonopah, Nev., from bore hole 2,316 feet deep. Bicarbonates were reduced to normal carbonates. R. C. Wells, analyst.

38. Nettie mine, Butte, Mont., 300-foot level. W. F. Hillebrand, analyst. Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 101, 1912.

39. Headquarters mine, Baguio, P. I., upper workings 20 meters from surface. Solution neutral to litmus., Aluminum is included with iron. Solution contains 1.6 cubic centimeters CO_2 per liter. V. Q. Gana, analyst. Eddingfield, F. T., Alteration and enrichment in calcite-quartz-manganese gold deposits in the Philippine Islands: Philippine Jour. Sci., vol. 8, No. 2, Sec. A, p. 127, 1913.

40. Headquarters mine, Baguio, P. I., upper workings 40 meters from surface. Solution contains 5.0 cubic centimeters CO_2 per liter. Solution neutral to litmus. V. A. Gana, analyst. Eddingfield, F. T., idem.

41. Colorado mine, Masbate, P. I. Reaction alkaline. V. Q. Gana, analyst. Eddingfield, F. T., idem.

DISCUSSION OF ANALYSES.

MINES REPRESENTED.

Of the foregoing analyses of 41 samples of water taken from mines containing sulphide deposits, samples 1 to 19 were taken from copper mines and samples 20 to 41 from gold, silver, and gold and silver mines. The tables include almost all the available nearly complete analyses of waters from sulphide deposits in noncalcareous rocks. Among those not included in the table are several analyses of waters from the district in southeastern Missouri containing disseminated lead deposits, discussed by Buckley,[1] and some analyses

[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties, Mo.: Missouri Bur. Geology and Mines, vol. 9, pt. 1, pp. 99, 171, 249, 1908.

of waters from the Granby district and from Joplin, in southwestern Missouri. A number of partial analyses of waters from gold mines of Australia and New Zealand are reported by Don,[1] and several analyses of waters from the Homestake mine, Lead, S. Dak., have recently been published by Sharwood.[2] Analyses of waters from the Lake Superior iron and copper mines and from the Joplin region, Mo., are given on pages that follow.

Six mines are represented by two or more analyses. More extended series of analyses of waters taken at different depths from the same body of water would be very useful in investigations made to determine the acidity and the state of oxidation of waters as related to depth. The first work of this character was done by Lepsius,[3] who showed that the oxygen content of waters taken from bore holes decreases with increase of depth. A series of samples (Nos. 13 to 16) from the different levels of the Capote mine, Cananea, Sonora, analyzed under the direction of G. W. Hawley, chief chemist of the Cananea Consolidated Copper Co., is especially valuable. Samples 11 and 12 were obtained from the Callaway shaft at Ducktown, Tenn.; sample 11 was taken from the top of the water level in this shaft, and sample 12 was taken 37 feet below. To obtain this sample a special device was arranged by Mr. Laney and myself for subaqueous filtration. This device consisted of a crate holding two 1-gallon bottles, below which was attached a heavy weight to sink the unfilled bottles; below this was attached, with a short rope, a second weight for sounding. Each bottle was equipped with a small cylindrical filter tube charged with asbestos wool. A perforated porcelain disk was placed below and another above the wool to equalize pressure. The filter tube extended nearly to the bottom of the bottle to prevent air from coming into contact with the water dropping into the bottles. Each stopper was fitted with a glass exhaust tube extending from the top of the bottle to a point above the filter, and the upper end of each tube was fitted with a valve which let out air but prevented any intake of water. Rubber sheeting was fastened over the filter to prevent premature entry of waters and this was removed by means of a strong cord passed to the surface. The bottles were lowered slowly to prevent the stirring of the water in the shaft.

Many of the samples were taken from small bodies of water standing in mines. The water in such bodies is generally more concentrated than the average water of the mines and is probably not

[1] Don, J. R., The genesis of certain auriferous lodes: Am. Inst. Min. Eng. Trans., vol. 27, p. 654, 1898.

[2] Sharwood, W. J., Analyses of some rocks and minerals from the Homestake mine, Lead, S. Dak.: Econ. Geology, vol. 6, p. 742, 1911.

[3] Lepsius, B., Ueber die Abnahme des gelösten Sauerstoffs im Grundwasser und einen einfachen Apparat zur Entnahme von Tiefproben in Bohrlöchern: Deutsch. chem. Gesell. Ber., vol. 18, pt. 2, pp. 2487–2490, 1885.

typical underground mine water. Samples 7, 8, 9, 10, 11, 12, 23, 28, 29, 34, 35, 37, and probably several others were taken from underground streams or rills or from large bodies of standing water.

The composition of mine water, especially that in the upper part of a deposit, is changed by the opening of the mine, by which, doubtless, the water is more highly oxidized and probably its acidity is increased. The addition of artificial water channels and the depression of the ground-water level by pumping produces mixtures of water from several levels and increases the rate of the underground circulation. This increase tends to dilute the waters; but, on the other hand, the downward change to a more highly oxidized and therefore a more highly acid condition will render the solutions more active solvents and tend to increase the concentration of metals they contain. Which set of processes predominates can not be shown, but the analyses represent only qualitatively the character of the solutions by which alterations of sulphide ores are brought about. Many of the analyses are not complete, and some analysts do not state whether certain elements were looked for. Some of the averages are therefore only rude approximations.

In the work of recalculating these analyses to the ionic form of statement I have had assistance from Messrs. H. K. Shearer, N. Sankowsky, and Clarence Russell.

CHEMICAL CHANGES INDICATED.

Sulphates and sulphuric acid.—Sulphides exposed to air and water are changed to sulphates and to sulphuric acid. The iron minerals are the more important sources of sulphuric acid because some of them contain more sulphur than that necessary to balance iron when iron sulphate forms and because iron sulphate in the presence of oxygen forms the ferric salt, which hydrolyzes readily, giving basic ferric sulphate and ultimately limonite. Galena and zinc blende may oxidize to sulphates without liberating acid. The following equations, which represent certain stages in the reactions, illustrate this principle:

$$FeS_2+H_2O+7O=FeSO_4+H_2SO_4.$$
$$Fe_7S_8+H_2O+31O=7FeSO_4+H_2SO_4.$$
$$CuFeS_2+8O=FeSO_4+CuSO_4.$$
$$PbS+4O=PbSO_4.$$
$$ZnS+4O=ZnSO_4.$$

The oxidation of ferrous sulphate to ferric salt and the hydrolysis of ferric sulphate take place very readily in the presence of oxygen.

$$2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O.$$
$$6FeSO_4+3O+3H_2O=2Fe_2(SO_4)_3+Fe_2(OH)_6.$$
$$Fe_2(SO_4)_3+6H_2O=2Fe(OH)_3+3H_2SO_4.$$

All the waters from copper mines (1–19) are sulphate solutions. Carbonates are determined in only two of these—No. 1, an alkaline water taken at some distance from any known ore body, and No. 19, also an alkaline water. The combined negative radicles of several are insufficient to balance the positive radicles, a fact that suggests the probability that some of the metals are balanced by carbon dioxide, hydroxyl, or silicic acid. The average sulphate (SO_4) of 19 samples of water from copper mines is 5,412.7 parts per million. This figure is increased greatly by sample 5, an exceptionally strong sulphate solution. The average sulphate of the 18 other samples is 1,820.9 parts per million. The average sulphate of 22 samples from gold and silver mines is 9,754.9 parts per million; if the sample of concentrated water (No. 24) from the Comstock lode is eliminated the average of 21 samples is 252.7. The average sulphate (SO_4) in the 41 waters is 7,839. In seven of the waters from copper mines the acidity has been determined, the average being 291 parts per million, calculated as sulphuric acid (H_2SO_4). Samples 7 and 8 show appreciable acidity, notwithstanding a deficiency of sulphate ions to balance the metals. In at least 16 samples there is no free acid. Of these at least 10 samples from copper and precious-metal mines (1, 2, 3, 4, 19, 28, 29, 34, 35, 41) are alkaline.

Chlorides.—The salt (NaCl) in sedimentary rocks may be dissolved by ground water, and in some places it is a source of commercial supply. From the available analyses it appears that in many regions the amount of salt in such rocks is small. The chlorine content of composite samples of 78 shales and 253 sandstones is only a trace, and an analysis of a composite of 345 limestones shows only 0.02 per cent.[1] A few rock-making minerals, such as chlorapatite, scapolite, haüyne, and nosean, contain combined chlorine; but all of these except apatite occur mainly in rocks of very rare types. In some rocks chlorine is present probably as sodium chloride in the solid particles contained in fluid inclusions.

Apatite, though widespread in igneous rocks, is a fairly stable mineral and consequently can not be regarded as an important source of chlorine, although it may afford small amounts when exposed to favorable conditions of weathering. The average chlorine content of igneous rocks, according to F. W. Clarke, is 0.06 per cent.

Chlorine is present in nearly all surface waters, which derive it from fine salt or salt water from the sea or other bodies of salt water. The fine salt is carried by the wind and precipitated with rain.[2] As

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 28, 1916.

[2] Jackson, D. D., The normal distribution of chlorine in the natural waters of New York and New England: U. S. Geol. Survey Water-Supply Paper 144, 1905.

shown by figure 10, the amount of chlorine in bodies of natural water varies with remarkable constancy with variations in the distance of the bodies from the shore. Several determinations of water from

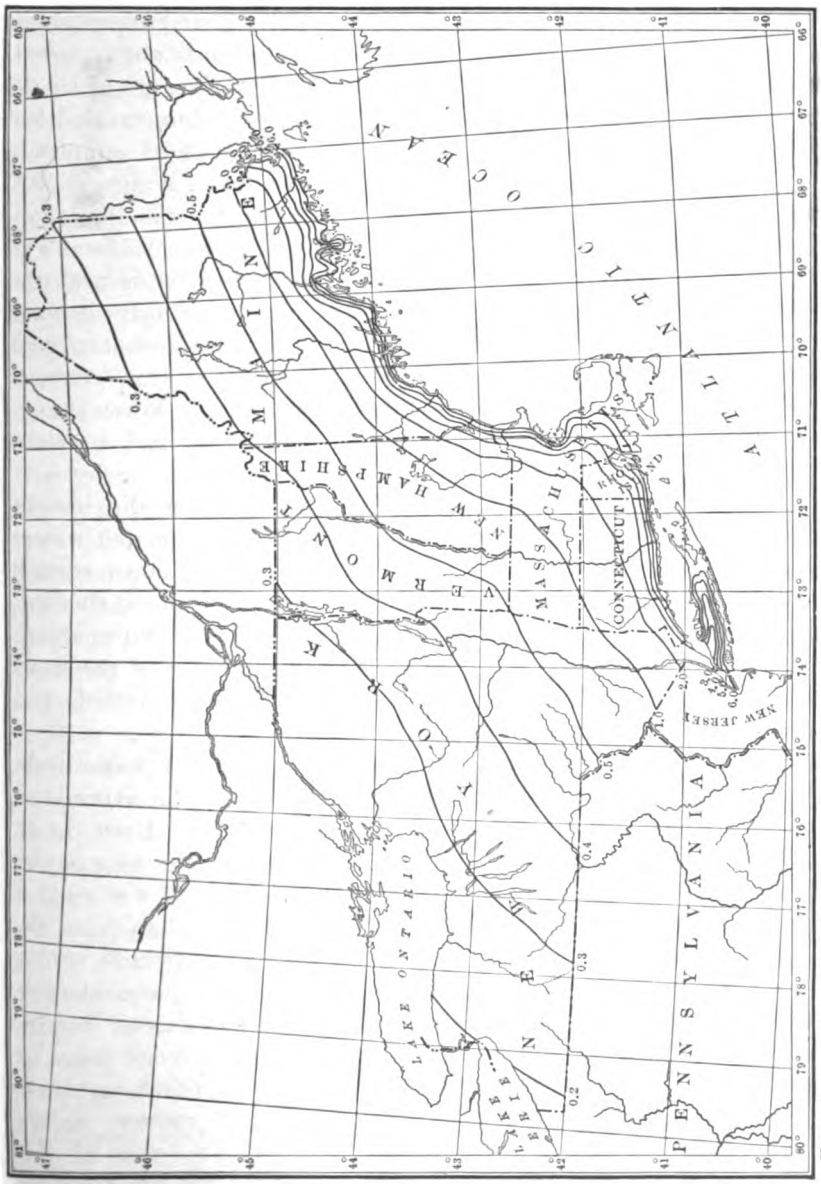


FIGURE 10.—Normal chlorine map of New England and New York. Figures on curve indicate parts per million. After D. D. Jackson.

bodies very near the seashore show 10 to 30 parts of chlorine per million; in bodies a few miles away it is generally about 6 parts per million; in bodies 75 miles from shore it is generally less than 1 part per million.

In arid countries dust containing salt doubtless contributes chlorine to mine waters. Penrose,[1] discussing the distribution of the chloride ores, pointed out long ago that chlorides form most abundantly in undrained areas.

The average chlorine content of the 19 waters from copper mines is 58.9 parts per million. In three of these chlorine is not reported, but in two of the three it was not looked for. The average of the 16 samples is 69.9. The waters from gold and silver mines carried less chlorine than those of copper mines. The average of 22 samples is 21.3. Exclusive of six samples showing traces, the average is 29.3.

The chlorine content of waters of well-drained areas like those of Ducktown, Tenn., and Creede, Colo., is conspicuously low. The amount of chlorine in deposits in or near arid regions or near the sea is greater. Two samples from Butte, Mont., show a large content of chlorine. In general the chlorine content in the samples analyzed is much lower than in samples of water obtained by Don[2] from a large number of Australasian mines and considerably lower than a former estimate (873 parts per million) given by me in a previous paper[3] on the concentration of gold by cold solutions.

Carbonates.—As sulphuric acid tends to drive carbon dioxide out of solution, it would not be supposed that highly carbonated waters would be common in oxidizing zones of mines where the ore carried much pyrite. That small amounts of sulphuric acid and carbonates may exist in the same solution is shown, however, by several analyses. In the acid waters under consideration the carbonates of the bases would necessarily be present as bicarbonates, although this fact is not indicated in all the analyses.

Carbonates were determined in only two samples of water from copper mines but are probably present in others. The average of those two is 83.3 parts per million. Carbonates are shown in 15 waters from gold and silver mines, the average of the 15 samples being 216.2 parts per million. The average of the 17 waters that carry carbonates is 200.5 parts per million. Two waters from the Geyser mine, Custer County, Colo., and two from Creede, Colo., contain, in addition to the carbonate radicle (CO_3), considerable excess carbonate calculated as carbon dioxide, but this is not included in the average. Several analyses of waters from mines of Butte, Mont., show insufficient carbon dioxide in the bicarbonate

[1] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, pp. 314–316, 1894.

[2] Don, J. R., The genesis of certain auriferous lodes: Am. Inst. Min. Eng. Trans., vol. 27, p. 654, 1898.

[3] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, p 9, 1912. See also Jour. Geology, vol. 19, p. 20, 1911. To obtain this estimate many partial analyses were included. These are not given in the table herein.

state to satisfy the bases, hence both normal and bicarbonates were assumed as present, and the summation was raised to correspond.[1]

Silica.—The analyses show that an appreciable quantity of silica is dissolved by even strongly acid mine waters. Very little is known concerning the conditions that favor the solution of silica in such waters. Solutions that contain much alkali and carbonate generally carry larger quantities of silica, although the one that carries the most silica is a concentrated sulphate solution from the Comstock lode. The average silica content of 19 waters from copper mines is 43.9, that of waters from 22 precious-metal mines is 60.8.

Arsenic and antimony.—Compounds of arsenic and antimony are dissolved in some mine waters, for there is evidence that minerals containing these metals are deposited from cold solutions. Only traces of antimony are reported in any analyses, but arsenic is more soluble and when hydrolyzed in acid solutions forms not only basic insoluble salts but the soluble acids. Hillebrand notes that considerable arsenic was found in a precipitate from a filtered sample of water collected by Lindgren at Grass Valley, Cal., where the gold ores carry arsenopyrite. Traces of arsenic are reported in three waters from Butte, Mont. A partial analysis[2] of another water from the Leonard mine records 2.6 parts of arsenic and 0.8 part of antimony per million. This is noteworthy, as the water carries 139 parts of free acid per million.

Nitrates.—Nitrates are not abundant in mine waters. In only one analysis (21) is nitrate (NO_3) reported (1.60 parts per million), and this in a water that was questionably representative, for it appears to have been imperfectly filtered.[3] A possible source of nitrate is dynamite, commonly used in mines.

Phosphates.—Traces of phosphate are reported in eight mine waters. One sample contained 1.5 parts per million; others contained none, or only traces, if determinations for phosphate were made.

Potassium.—Potassium has been found in all the samples of mine waters from copper mines where it was looked for. The average of 14 samples is 10.7. In the samples from gold and silver mines it ranged from 1 part to 254 parts per million, the average of 14 samples being 53.9.

Sodium.—Owing to its greater solubility in sulphate solutions, sodium is generally more abundant than potash in these mine waters. The 14 samples of waters from copper mines in which sodium was

[1] Hillebrand, W. F., Composition of mine waters, in Weed, W. H., Geology and ore deposits of the Butte district, Mont.: U. S. Geol. Survey Prof. Paper 74, p. 101, 1912.

[2] Min. and Sci. Press, vol. 105, p. 404, 1912.

[3] Emmons, S. F., The mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 462, 1896; analysis of water from Geyser mine, Silver Cliff, Colo. See also statement of W. F. Hillebrand, analyst, on p. 460 of same report.

determined averaged 34.4. The average sodium content of 14 samples of water from precious-metal mines is 122.9 parts per million.

Calcium.—The average calcium content of 19 samples of waters from copper mines is 204.9 parts per million. The average of 22 samples of waters from precious-metal mines is 136.2 parts. Calcium was determined in every sample.

Magnesium.—In 18 samples of waters from copper mines magnesium averages 47.4 parts per million. In 18 samples of waters from precious-metal mines it averages 397 parts. In 4 samples of such waters it is not reported. The remarkable concentration of magnesium in sample 24 (an exceptional water) brings the average far above that of calcium, but notwithstanding the greater solubility of its sulphate, magnesium exceeds calcium in only three of the samples.

Aluminum.—Like the alkalies and alkaline earths, aluminum is readily dissolved from the silicates of the ore or from the wall rock. In general, it is more abundant in sulphate waters than in those that carry considerable carbonate. It is not present in the alkaline waters.

The average aluminum in 12 samples from copper mines is 81.5 parts per million. It is absent in 4 waters from mines at Butte, Mont., which are in "granite." All these waters give alkaline reactions. Aluminum is reported from only 8 samples of water from precious-metal mines, the average being 1,209.9. If analysis 24, which shows exceptionally high alumina, is excluded, the average of the 18 other samples is only 1.3 parts per million.

Manganese.—In 16 samples of water from copper mines the average content of manganese is 40.8 parts per million. In two analyses it is not reported; in another a trace is shown. It is especially abundant in the waters from Cananea, Sonora, Mexico.

The average of 13 samples of water from precious-metal mines is 81.5 parts per million. It is not reported in 8 samples. The variation in manganese content is exceedingly great. Only two waters—one from the Comstock lode and another from the Stanley mine, Georgetown, Colo.—contain more than a few parts per million.

Iron.—All the 19 samples of water from copper mines contain iron. In 2 analyses it is stated as total iron. In 15 samples ferrous iron is present, the average of these being 283.5 parts per million. Ferrous iron present in 20 samples of the 41 averages 210.9 parts per million. There is ferric iron in 7 samples of copper mine waters, in which it averages 55.9 parts per million. It is present in 6 waters of precious-metal mines, in which its average is 841.3 parts per million. In the 13 analyses of all waters that carry ferric iron the average is 418.2 parts per million. None of the analyses of samples taken underground at Cananea (Nos. 13–16) show ferric iron, yet the sample (17) taken from the concentrator, where it circulates over the tables in contact with ore and air, contains appreciable ferric iron.

In 2 samples of water from precious-metal mines iron is stated as total iron. Acid waters carry much more iron than alkaline waters, in which, as would be supposed, little or no ferric iron is found.

If sample 24 from the Comstock lode is excluded, the average of the other 5 samples is only about 5 parts per million. This is lower than the ferric iron in waters from copper mines and very much lower than the ferric iron determined by Don in many waters from Australasian mines.

Copper.—Copper, dissolved as sulphate, is abundant in many mine waters. In some mines at Butte, Mont., Ducktown, Tenn., Jerome, Ariz., and Rio Tinto, Spain, and in the Ballygahan mine, Wicklow, Ireland, the waters during certain periods of development have been sufficiently cupriferous to yield marketable quantities of copper. The average of 13 samples from copper mines is 3,690 parts per million. In 6 samples it is absent or is not reported. The water from the Mountain View mine at Butte, Mont., is by far the most highly cupriferous. Exclusive of this, the average of 12 samples is only 195.5 parts per million. Copper is reported also in a concentrated water from the Comstock lode (No. 24) and in water from the Stanley mine at Georgetown, Colo. (No. 36), and traces are present in waters from other precious-metal mines (20 and 21).

Zinc.—The zinc content of the waters of 15 copper mines averages 140.3 parts per million. The average of 22 samples from precious-metal mines is 5.8 parts per million. In the 7 of these from which it is reported the average is 18.3 parts per million. Some waters from mineral deposits of the Mississippi Valley contain abundant zinc.

Gold and silver.—Small amounts of gold and silver have been detected in waters from the Comstock lode,[1] and gold has been determined in a water from the Homestake mine, in South Dakota.[2] Traces of both gold and silver are present in waters from the Granite vein, Philipsburg, Mont.

CHANGES IN COMPOSITION DEPENDING ON DEPTH.

Waters descending from the surface through sulphide ore deposits pass through a changing chemical environment and are continually changing in chemical composition. In the oxidized zone, as already stated, they are oxidized waters and acid waters; when they pass below the region where oxygen is in excess their acidity and their state of oxidation change. Their reaction on some sulphides produces hydrogen sulphide, and their reaction on silicates and car-

[1] Reid, J. A., The structure and genesis of the Comstock lode: California Univ. Dept. Geology Bull., vol. 4, pp. 189, 192, 1906.

[2] Sharwood, W. J., Analyses of some rocks and minerals from the Homestake mine: Econ. Geology, vol. 6, p. 742, 1911.

bonates decreases their acidity. Iron is generally abundant in waters of pyritic ore bodies, and the degree of the oxidation of the iron is important as an index to the state of oxidation of the water. Mineral waters may thus be divided into several groups, depending on the degree of their oxidation and their acidity. Nos. 8, 9, and 10 from Ducktown, Tenn., are samples of waters containing sulphuric acid and ferric sulphate. Samples of sulphuric acid and ferrous sulphate water are represented by No. 18, from the Ruth mine, Ely, Nev.; Nos. 7, 11, and 12 from Ducktown, Tenn.; No. 36, from the Stanley mine, Georgetown, Colo.; and No. 33, from the Rothschönberger Stolln, Freiberg, Germany.

Of the 41 samples of water analyzed 16 or more carry no free acid, and 10 of these are alkaline. The alkaline waters include two (34, 35) from the deep levels of mines at Creede, Colo., where they descended to depths of 1,300 feet or more before they issued at the drain levels. As would be supposed, ferric iron is not present in any of the analyses of alkaline waters.

Samples 28 and 29 are waters collected by Waldemar Lindgren from the 400-foot levels in the Federal Loan and Black Prince mines at Nevada City, Cal. As the temperature of these waters when collected was the same as that of the surrounding rock, they come, presumably, from the meteoric circulation. Both are alkaline and both form yellow-brown deposits consisting principally of hydrated iron oxide, alumina, and silica. These waters were clear when bottled, but when opened after several months both contained dark-colored deposits of silica, hydroxides, and sulphides. Dr. W. F. Hillebrand, who made the analyses, detected no hydrogen sulphide in either water, although both appeared to contain a little thiosulphate. Sample 28 contained metallic sulphides in solution, and an odor of hydrogen sulphide was noticeable near the place where it was obtained. Sample 29 contained no metallic sulphides and emitted no noticeable odor of hydrogen sulphide. At least eight additional samples (7, 8, 9, 10, 11, 12, 34, and 35) have been tested for hydrogen sulphide, with negative results. Sample 2 deposited sulphur and ferrous sulphide.

Although hydrogen sulphide is rare in mine waters, it forms when certain sulphides are in contact with acid. When exposed to the air it oxidizes rapidly. It is not supposed that it would accumulate, at least not in the zone where air has free access to the deposits, where most samples of mine waters are taken. On descending to greater depths it would be used up according to the reaction—

$$Fe_2(SO_4)_3+H_2S=2FeSO_4+S+H_2SO_4,$$

or it may be used up also in the precipitation of metallic sulphides from sulphates. Whether it would be used first to form ferrous sulphate and afterward to precipitate metallic sulphides can not

be shown, but this order of action occurs at least under some conditions. Samples 7 and 8 from Ducktown, Tenn., are especially instructive in this connection, for No. 7 contains much ferrous iron and no ferric iron, whereas No. 8 contains much ferric iron and only 1.3 parts of ferrous iron. The ore through which sample 7 passed before issuing where it was taken is more than 90 per cent pyrrhotite, which generates hydrogen sulphide rapidly. The ore through which sample 8 passed contains chiefly chalcopyrite and lime silicates, with but little pyrrhotite. This water contains considerable iron, almost all in the ferric state. Since No. 7 contains even more copper than No. 8 it appears that the ferric sulphate is reduced to ferrous sulphate ($FeSO_4$) before copper sulphide is precipitated, as in this water the iron is entirely reduced to the ferrous state while there is still a considerable amount of copper in solution. It is noteworthy that the alkaline waters contain appreciable quantities of carbonates, with lime, potash, and soda. They carry also a certain concentration of sulphates. Of the alkaline waters two from Nevada City, Cal., and two from Creede, Colo., have descended through considerable unoxidized material. Alkaline waters have not received sufficient attention in studies of sulphide enrichment.

Samples 13, 14, 15, and 16 are from the Capote mine, at Cananea, Mexico. The deposit is in an area of quartzite and other rocks intruded by diorite porphyry. The ore is in part of the disseminated type and carries pyrite, chalcopyrite, and zinc blende, with secondary chalcocite. I can not state the vertical range of chalcocite in this deposit, but it is not so abundant at the 900-foot level, where sample 15 was obtained, as it is at the 300-foot level, where sample 13 was obtained. Sample 13 contains 970 parts of free acid per million, whereas the samples taken at greater depths contain no free acid.

The two pairs of samples Nos. 9 and 10 and Nos. 11 and 12 are from unused shafts at Ducktown, Tenn. As stated above, the samples 10 and 12 were taken by lowering bottles equipped with asbestos filters to the desired depths, then removing the covers from the filters and allowing the bottles to fill. The waters from the open shafts are diluted by a large proportion of surface water, so they are less concentrated than mine waters that have traveled considerable distances through the rocks. In taking samples 9 and 10 the water was disturbed, so that the analyses of these samples are of less value; samples 11 and 12 were taken with special precautions to prevent agitation and show very well the difference in the mineral content of the waters at different depths. The water from the water level (No. 11) contains more than twice as much free acid as the deeper water, No. 12, taken 37 feet deeper. No. 12, taken below water level, is more concentrated with respect to

silica, calcium, magnesium, aluminum, zinc, and iron, but the concentrations of potassium, sodium, and manganese are closely similar. The amount of copper is greatly decreased. This suggests that at a depth of 37 feet other metals are being taken into solution, but the greater part of the copper has already been deposited. Although the deeper water contains more ferrous iron and more ferric iron than that at the water level, the proportion of ferric to ferrous iron has increased with increase of depth, showing just the reverse of the conditions expected. It is thought that the increase in the proportion of iron in the solution with increase of depth has been brought about by reaction of acid on pyrrhotite, and also that ferric iron has decreased near the surface by hydrolysis of ferric sulphate. The filter paper was colored red by a dustlike iron precipitate, probably basic ferric sulphate, formed presumably near the surface and held in suspension in the water. The formation of this precipitate probably accounts for the very small concentration of ferric iron at the surface of the standing water, and possibly also for the somewhat smaller amount of total sulphate held in solution near the surface. This precipitate would probably not form so extensively under conditions affording free circulation.

The four waters from Freiberg, Germany (samples 30, 31, 32, 33), agree in containing considerable zinc and manganese. One of them on standing forms a deposit consisting chiefly of manganese oxide and some zinc oxide.

Sample 21 is from the 2,000-foot level of the Geyser mine at Silver Cliff, Colo. This water contained some nitrate, which is uncommon in analyses of mine waters.

Several of these waters do not contain sufficient amounts of the negative radicles to hold in solution the metallic portions. If carbon dioxide was determined in such waters, a part of the metals must be dissolved as silicates or possibly even as hydroxides.

PRECIPITATES FROM MINE WATERS UNDER SUPERFICIAL CONDITIONS.

Many waters, after issuing from mineralized rocks, deposit copious precipitates, and some such deposits are so large that the mine workings have been closed by them. (See Pl. III.) In some mining districts the streams which carry away the underground drainage from the adits have stained their beds for great distances from the points of issue. In certain of these areas, as at Cananea, Mexico, near Homestake mine, South Dakota, and at Bingham, Utah, the gravels above the present streams are cemented by iron oxides, showing that the processes of precipitation at the surface were operative before the mines were opened. These deposits, formed under atmospheric pressure and in the presence of oxygen, are very different

STALACTITES OF LIMONITE, SILVERBOW MINE, BUTTE, MONT.

After W. H. Weed.

from the deposits of secondary ore that are formed at depths where sulphide enrichment is assumed to take place. Few, if any, of them are workable for the more valuable metals. Nearly all of them consist largely of the colloidal compounds, such as the hydrous iron oxides, hydrous aluminum compounds, and hydrous silica.

Many samples of water quickly become cloudy after they have been filtered, either because of oxidation by air, or because of slight changes in temperature, or because of loss of carbon dioxide or some other gas by agitation; or, if they have been taken from low depths, because of decrease in pressure. Two samples of water taken from adits at Creede, Colo., and filtered in the presence of air deposited light-gray precipitates, presumably compounds of aluminum and silica. Six samples collected at Ducktown, Tenn., were likewise clouded. Two of these samples, one taken 37 feet and the other 55 feet below the water level, were filtered under water, and although the air spaces left in the necks of the bottles were exceedingly small the samples clouded in a few hours. Several samples from Butte, Mont., deposited solids before analyses were made.

The results of analyses of six samples of material precipitated from mine waters are stated in the table below. Sample 1 is from a water in the Stanley mine, near Georgetown, Colo. (No. 36 in table above). Sample 2 is from a mine in Freiberg, Saxony. The sample was taken from workings that had been flooded 135 years. It contained much manganese and considerable zinc. Sample 3 is a slime collected in the Federal Loan mine,[1] near Nevada City, Cal., where the water represented by sample 28 of the table on page 88 issued from the wall rock. Of this analysis Dr. Hillebrand makes the following remarks:[2]

> The bottle was filled with a black slimy matter emitting a disgusting odor of organic decomposition. The cork was forced out with ease by imprisoned gas, chiefly consisting of CO_2 and CH_4. The slime was said to have been white when collected; the subsequently developed black color is due to iron sulphide. Aside from organic matter and water, the deposit is essentially ferric oxide with a little arseniate, calcium carbonate with a little magnesium carbonate, and manganese as MnO_2, besides gelatinous silica and fragments of minerals.

A deposit collected by Lindgren in the drain tunnel of the Providence mine, near Nevada City, Cal., when dried, formed dirty white masses and coarse green lumps. An analysis of some of the green pieces is given in column 4 of the following table. Samples 5 and 6 are from the Geyser mine, Custer County, Colo.:

[1] Lindgren, Waldemar, The gold quartz veins of Nevada City and Grass Valley districts, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 121, 1896.

[2] Idem, pp. 122–123.

Analyses of muds precipitated from mine waters.

	1	2	3	4	5	6
SiO_2	10.85	[a] 3.55	18.4	8.31	[a] 0.08	[a] 0.10
Al_2O_3	2.87	.....	.....	37.57	.....	.....
Fe_2O_3	53.57	7.78	23.3	.44	.2	1.08
FeO	.....	.....	.....	.....	.....	.....
MnO_2	.....	[b] 53.21	.6	.....	[c] .03	[c] .03
CaO	.....	.....	10.8	.12	53.11	52.6
MgO	.....	.....	.....	Trace.	1.5	1.4
Pb	.....	.....	Trace.	.....	.....	.....
CuO	.....	3.20	.....	.57	.....	.....
ZnO	.....	6.08	.....	.....	.....	.....
Mo	.....	.....	.....	Trace.	.....	.....
As	.....	.....	1.3	.....	.....	.....
Na_2O	.....	.....	.....	.17	.....	.....
SO_3	11.46	.67	.5	9.51	.29	.5
H_2O	21.14	19.99	34.9	42.98	1.21	1.23
CO_2	.....	.....	.....	.....	42.98	42.57
	99.89	[d] 99.48	99.8	99.67	[d] 99.76	[d] 99.95

[a] Insoluble residue.
[b] Some MnO present. The analysis as stated gives O, 8.43, and MnO, 44.78.
[c] Mn_2O_3?
[d] With additions noted below.

1. Precipitate filtered from water of Stanley mine. Jones, L. J. W., Ferric sulphate in mine waters and its action on metals: Colorado Sci. Soc. Proc., vol. 6, p. 48, 1900.

2. Deposit from a mine at Freiberg, Saxony, taken from workings that had been flooded 135 years. Contains cobalt oxide, 1.36; cadmium oxide, 0.19; lead oxide, 3.45. Beck, Richard, Lehre von den Erzlagerstätten, p. 402, 1901.

3. A deposit from water from Federal Loan mine, near Nevada City, Cal. CaO equals $CaCO_3$ and $MgCO_3$; organic material calculated with water. Insoluble material included with SiO_2. Lindgren, Waldemar, The gold quartz veins of Nevada City and Grass Valley districts, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 122, 1896.

4. Part of deposit in drain tunnel of Providence mine, near Nevada City, Cal. Lindgren, Waldemar, idem, p. 123.

5. Deposits of sinter from 2,000-foot level of Geyser mine, Custer County, Colo. Emmons, S. F., Mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, pp. 459–460, 1896. W. F. Hillebrand, analyst. Shows ripple-marked structure. Contains also SrO, 0.17; K_2O, 1.5; and Na_2O, 0.17, with traces of phosphorus, chlorine, and lithium and minute traces of lead, copper, nickel, cobalt, zinc, and aluminum.

6. Deposits of sinter from 2,000-foot level of Geyser mine, Custer County, Colo. Emmons, S. F., idem. Contains also SrO, 0.26; K_2O, 0.03; and Na_2O, 0.16. Traces of metals noted in 5 also noted in 6. A third analysis from the same depth is of pisolitic sinter.

COMPOSITION OF MINE WATERS OF THE JOPLIN REGION.

The table on page 103 gives analyses of mine waters of the Joplin district, Missouri. The deposits are iron, lead, and zinc sulphides, inclosed in cherty limestone. They contain also some sulphides of copper and cadmium. These waters closely resemble those obtained in mines of lode ores in the Western States. They are strong sulphate solutions, containing much zinc and some cadmium. In view of the fact that the deposits are in calcareous rocks the acidity is noteworthy.

Analyses of mine waters of the Joplin district, Missouri.

	42	43	44
SO_4	6,153.2	1,647.6	2,728.4
Cl	2.7	3.7	6.8
CO_3	.....	.....	.....
SiO_2	107.6	23.2	36.4
K	.5	3.2	4.2
Na	49.9	13.0	48.2
Ca	345.3	260.5	608.6
Mg	25.2	48.6	57.6
Al	142.1	11.7	8.4
Mn	1.7	.....	3.4
Cu	3.7	.....	Trace.
Zn	2,412.0	345.1	454.5
Cd	9.0	.....	.8
Fe''	} 474.6	142.8	274.7
Fe'''			
Free H_2SO_4	.....	251.7	.....

42. Alabama Coon mine, Joplin district, Missouri. H. N. Stokes, analyst.
43. Victor mine, Joplin district, Missouri. H. A. Buehler and V. H. Gottschalk, analysts.
44. Water from Missouri zinc region. H. N. Stokes, analyst.

In order to compare the mine waters in lode deposits with the waters of a deep circulation through rocks containing small amounts of lead, zinc, and iron sulphide, I have rearranged and give on page 104 a table of analyses recently presented by C. E. Siebenthal. As in previous tables, iron and aluminum are stated as Fe and Al, instead of as oxides of these metals, and CO_3 instead of HCO_3 ion as stated by Siebenthal.[1]

The Joplin region is on a great monocline that dips at a very low angle westward from the Ozark uplift. Along the northwest border of the region the older Paleozoic limestones, cherts, and sandstones are capped by Pennsylvanian shale, but about the crest of the Ozark uplift Carboniferous rocks are eroded away so as to expose the edges of the Ordovician and Cambrian rocks. Waters entering these older rocks pass downward and outward, and where wells or other openings penetrate the Pennsylvanian shale the waters, having passed through great bodies of sedimentary rock, rise to the surface. These waters are believed by Siebenthal to have deposited ores of lead and zinc. They carry an average of 602 parts per million total solids, iron and aluminum being calculated as oxides. This amount is less than that of the average mine water but greater than that carried by the waters of some mines. The waters are neutral or very slightly alkaline. They carry considerable alkaline chlorides, carbon dioxide, and hydrogen sulphide. The metals are dissolved partly as bicarbonates, and when the waters are passed into basins at the surface sulphides of the metals and calcium carbonate are deposited as a result of escape of part of the carbon dioxide and hydrogen sulphide. Analyses of precipitates from such waters are given on page 104.

[1] Siebenthal, C. E., Spring deposits at Sulphur Springs, Ark., with a microscopic examination by H. E. Merwin: Econ. Geology, vol. 9, pp. 758–767, 1914.

Analyses of sediments from springs at Sulphur Springs, Ark.

[W. George Waring, analyst. Expressed in percentages of the total dried residues.]

	White Sulphur Spring.	Black Sulphur Spring.
Zinc	0.388	0.022
Lead	.040	.009
Copper	.005	.004
Iron	2.100	2.940
Sulphur	1.450	2.820
Lime	19.810	1.300
Magnesia	1.530	.100
Silica and insoluble silicates	49.930	62.820

Microscopic examination by Merwin of the sediments from Sulphur Springs, Ark., showed the presence of pyrite and calcite.

Analyses of deep waters in Joplin zinc-lead region.

[Parts per million.]

	45	46	47	48	49	50
SO_4	63.4	14.7	.....	12.5	6.0	11.4
Cl	315.8	126.9	141.4	142.7	106.1	95.3
CO_3	183.2	73.8	174.2	77.2	74.1	138.0
SiO_2	4.0	9.0	11.0	8.0	9.0	12.0
K	36.2	Trace.	.....	39.8	.....	.....
Na	294.4	126.9	141.4	88.0	94.1	106.7
Ca	133.6	58.9	128.67	60.7	52.9	77.6
Mg	100.7	31.2	48.4	42.5	40.5	63.7
Al	.....	.....	.....	1.6	.....	2.1
Fe	.....	.7	.....	.7	.....	1.6
CO_2	(?)	2.0	22.0(?)	6.0	3.0	(?)
H_2S	1 0	2.0	Strong.	Present.	Present.	Present.

45. Clinton, Mo., well; A. E. Woodward, analyst.
46. Chapman & Lennan mine; W. G. Waring, analyst. Sample taken Sept. 12, 1912.
47. Chapman & Lennan mine; W. G. Waring, analyst. Sample taken Dec. 23, 1913.
48. White Sulphur Spring; W. G. Waring, analyst.
49. Miami, Okla., well; J. F. Wexford, analyst.
50. Sulphur Spring; A. E. Meade, analyst.

COMPOSITION OF WATERS OF LAKE SUPERIOR MINES.

The table on page 106 gives six analyses of water from Lake Superior mines. Five of these are from iron mines and one (56) is from the Quincy copper mine. The first three are from shallow or moderate depths; the last three from great depths. Although the first three are very dilute solutions they appear to be capable of enriching iron ores somewhat by removal of valueless materials. They are alkaline and alkaline earth carbonate solutions with a little sulphate radicle, and one carries chloride. That such solutions remove silica is shown by the relatively high percentage of silica in their total solids. A little alumina has been dissolved by one solution and but little iron. These waters are dilute, and if such solutions leached so extensively the great bodies of thoroughly oxidized ores with which they are associated the leaching must have required eons of time. In the

earlier stages of oxidation, when the rocks contained more soluble materials, the mineral waters passing through them were probably more concentrated. It may be recalled here that some of the Lake Superior iron ores were exposed to weathering during much of pre-Cambrian and through a large part of post-Cambrian time.

The last three analyses from the deep levels of Lake Superior mines indicate very concentrated solutions of sodium and calcium chlorides, which drip in small quantities from rocks at great depths. Lane[1] considers them connate waters, or sea waters trapped when the rocks containing them were formed. The waters obtained near the surface are of the vadose circulation. They are more dilute, much more abundant, and are carbonate rather than chloride waters. Lane recognizes also waters of intermediate composition, doubtless mixtures of the two kinds of waters. Van Hise and Leith,[2] however, consider the deep concentrated chloride solutions "to be related to depth and stagnancy." They "must be regarded as representing solutions from which all possible insoluble materials have already crystallized out." The problem of these waters is perplexing. The explanation last stated meets difficulties in accounting for the abnormally high chlorine content; the other explanation appears to account for facts observed in the Lake Superior copper deposits, but does not appear to be applicable to high chlorine waters in iron deposits supposed to have been concentrated by circulation of meteoric water, for such waters should early have diluted and removed any connate water present. A third explanation might be suggested, namely, that the iron deposits, after they were deeply weathered and enriched, were sunk below the sea and the pore spaces filled with sea water, some of which still remains. Many of the Lake Superior deposits, as shown by Van Hise and Leith, were submerged after they had been deeply weathered, for they are capped by basal conglomerates of iron ore. The increase with depth of the ratio of calcium chloride to sodium chloride appears difficult to account for[3] by any of the explanations offered and suggests the desirability of more experiments with rocks and salt solutions, to be carried on in the cold for long periods of time.

[1] Lane, A. C., The Keweenawan series of Michigan: Michigan Geol. and Biol. Survey, Geol. ser. 4, vol. 2, p. 846, 1911.

[2] Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 544, 1911.

[3] A liter of water at 18° C. dissolves 5.42 mols NaCl; a liter of water at 18° C. dissolves 5.4 mols $CaCl_2$. In a sodium chloride water in contact with calcite concentration of lime chloride would probably increase.

Analyses of waters from Lake Superior mines.

[Parts per million.]

	51	52	53	54	55	56
SO_4	2.2	43.0	5.1	1,045.0	370.0	21.2
Cl			16.0	25,360.0	3,050.0	134,916.7
CO_3						21.2
SiO_2[a]	22.4	5.8	12.2			21.2
K	1.0	Not det.				
Na		Not det.	2.8	7,290.0	(?)	11,952.5
Ca	10.1	60.3	25.3	7,902.0	810.0	65,345.9
Mg		37.7	9.2	566.0		21.2
Mn				Trace.		
Al_2O_3		4.4		700.0		
Fe''	.0	Trace.	1.2			
Fe'''	.0					
CO_3	71.0	37.3	5.1	Not det.		

[a] Clay is included with SiO_2.

51. Drift between Hull and Rust mines, Hibbing, Minn. C. K. Leith, The Mesabi iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 43, p. 264, 1903.
52. Vulcan mine, 15th level, Menominee district, Michigan. E. E. Ware, analyst. Lane, A. C., The Keweenawan series of Michigan: Michigan Geol. Survey, Geol. ser. 4, vol. 2, p. 781, 1911.
53. Aurora mine, 900 feet deep, Ironwood, Gogebic Range, Mich. Idem, p. 783.
54. Republic mine, Mich., 1,710-foot level. G. Fernekes, analyst. Idem, p. 787. Water is a small drip.
55. Republic iron mine, Mich., 28th level, a slow drip. M. A. Cobb, analyst. Idem, p. 787.
56. Quincy copper mine, Mich., a deep level. George Steiger, analyst. Reported by Clarke, F. W., U. S. Geol. Survey Bull. 616, p. 185, 1916.

EXPERIMENTAL DATA ON THE SOLUTION AND PRECIPITATION OF THE METALS.

Under this heading are stated experimental data that bear upon superficial alteration and enrichment of ore bodies in general. On pages that follow may be found chemical data relating to each metal. The solutions that are the principal agents of alteration are the sulphates and carbonates, and subordinately also chlorides, silicates, and, perhaps, hydroxides and sulphides.

Sulphate solutions form by the oxidation of pyrite and other iron sulphides and subordinately by oxidation of sulphides of other metals. The oxidation of pyrite is considered by many to proceed as follows:[1]

$$FeS_2+7O+H_2O=FeSO_4+H_2SO_4.$$

This equation does not express intermediate steps, nor does it represent the final products. Ferrous sulphate in the presence of atmospheric oxygen will be oxidized to ferric sulphate or to ferric sulphate and ferric hydroxide:

$$6FeSO_4+3O+3H_2O=2Fe_2(SO_4)_3+2Fe(OH)_3.$$

The hydrolysis of ferric sulphate may first give a basic ferric sul-

[1] Allen, E. T., Sulphides of iron and their genesis: Min. and Sci. Press, vol. 103, pp. 413–414, 1911. Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides: Econ. Geology, vol. 7, pp. 15–34, 1912.

phate,[1] but this subsequently breaks down, forming ferric hydroxide and sulphuric acid, as indicated below:

$$Fe_2(SO_4)_3+6H_2O=2Fe(OH)_3+3H_2SO_4.$$

Ferric hydroxide probably corresponds to the mineral limnite, which on dehydration would give limonite:

$$4Fe(OH)_3=2Fe_2O_3+6H_2O=2Fe_2O_3.3H_2O+3H_2O.$$

According to Stokes[2] the oxidation of pyrite by ferric sulphate should be regarded as taking place by two independent reactions:

(1) $FeS_2+Fe_2(SO_4)_3=3FeSO_4+2S.$
(2) $2S+6Fe_2(SO_4)_3+8H_2O=12FeSO_4+8H_2SO_4.$

In the presence of air the ferrous sulphate formed would change again to ferric sulphate. But if ferric sulphate is limited and air has not free access to the solutions the attack of ferric sulphate may take place without increase of acidity. Experiments by Nishihara,[3] in which ferric sulphate was in contact with pyrite for seven days in stoppered bottles, showed steady decrease of acidity. With pyrrhotite the solution became neutral at the end of two weeks, when evolution of hydrogen sulphide gas ceased and hydroxide of iron had begun to form. A possible reaction in this case may be that indicated by the following equation:

$$Fe_7S_8+6Fe_2(SO_4)_3+H_2SO_4=H_2S+19FeSO_4+7S.$$

A. N. Winchell[4] treated powdered pyrite containing a trace of copper to dripping aerated water. At the end of ten months 300 grams of pyrite had lost 0.2 gram and the solution circulating through the pyrite had gained, per liter of the solution, the amounts indicated below:

	Milligrams.
$Fe_2(SO_4)_3$	27.68
H_2SO_4	5.7
Ferrous iron	Trace.
SO_3	Trace.

In the total solution there was—

	Milligrams.
$Fe_2(SO_4)_3$	332
H_2SO_4	68

Grout[5] repeated these experiments, subjecting the powdered mineral to repeated drying. In a year the specimens had lost from 0.015

[1] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 293, 1894. Brauns, Reinhard, Chemische Mineralogie, p. 368, Leipzig, 1896.
[2] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 15, 1901.
[3] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 749, 1914.
[4] Winchell, A. N., The oxidation of pyrite: Econ. Geology, vol. 2, pp. 290–294, 1907.
[5] Grout, F. F., The oxidation of pyrite: Econ. Geology, vol. 3, pp. 532–534, 1908.

to 0.057 per cent. These losses are of the same order as those shown by the figures obtained by Winchell, namely, 0.067 per cent.

Buehler and Gottschalk[1] made numerous experiments with distilled water, leaching powdered sulphides to determine the nature of the alteration products. The finely powdered sulphides were placed upon filter paper spread upon a Hirsch filter plate, which was fitted in a 6-centimeter funnel. The sulphides were then washed twice daily with distilled water, the filtrate being caught in a flat-bottomed flask. The sulphides were treated alone and also when mixed with pyrite or marcasite or some other natural sulphide.

A series of the filtrates obtained from marcasite alone and from marcasite mixed with galena, sphalerite, and copper sulphides were tested for free sulphur dioxide, sulphites, and thiosulphates, but none of these compounds were present.

In experiments with pyrite the residue left on the funnel was treated with carbon disulphide to test for the presence of free sulphur. No sulphur was found in a series of eight experiments, but a 10-pound sample of marcasite similarly treated showed the presence of free sulphur.

Tests for the presence of hydrogen sulphide as a possible decomposition product of these sulphides were made in an apparatus through which air could be drawn. The air was passed slowly through lead solution to free it from any hydrogen sulphide; it was then passed through a tube in which finely ground sulphide was placed; finally the air was again washed in lead solution. The sulphides were washed twice daily with water. After four months' continuous treatment there was no sign of blackening of the lead solution, indicating the absence of even traces of hydrogen sulphide. If any hydrogen sulphide had formed it was held in watery solution and oxidized before analysis. The following analysis of the solution and precipitate in the flask indicates hydrolysis:

Solution, 1,068 cubic centimeters.

$FeSO_4$, 0.0602 gram; $Fe_2(SO_4)_3$, 0.1799 gram; SO_3 (excess), 0.2697 gram; Fe_2O_3 (in the precipitate), 0.0218 gram.

The conclusion of Gottschalk and Buehler is that the oxidation of pyrite in water proceeds according to the reaction—

$$FeS_2+7O+H_2O=FeSO_4+H_2SO_4.$$

This does not involve the generation of hydrogen sulphide, of sulphur dioxide, or of more than an exceedingly small amount of sulphur.

[1] Buehler, H. A., and Gottschalk, V. H., Oxidation of sulphides: Econ. Geology, vol. 5, pp. 28–35, 1910; vol. 7, pp. 15–84, 1912.

In this connection it is noteworthy that these experiments were carried on with distilled water with very free access of air. Dilute acid solutions acting upon some sulphides of lead and zinc and upon ferrous iron will generate hydrogen sulphide.

In several experiments by Gottschalk and Buehler[1] the powdered sulphides spread on a filter were washed twice daily with distilled water. In most of these experiments the sulphates were passed through 60-mesh screens and caught on 80 or 100 mesh screens, so that the powders were of approximately equal fineness. In some experiments galena was caught on 200-mesh screens, giving relatively greater surfaces for attack. Equal masses, not equal volumes, of the several minerals were taken.

In most experiments the accumulated washings were about 500 cubic centimeters. Pyrite, marcasite, galena, sphalerite, and enargite were attacked. Each of the metals was oxidized to sulphate and washed through the filter. Pyrite and marcasite were oxidized to ferric and ferrous sulphate and to sulphuric acid. Zinc sulphide was oxidized to zinc sulphate and washed through. Galena was oxidized to lead sulphate, but most of it remained on the filter, though some washed through; of the part that washed through a little was deposited in the flask as lead sulphate. Hydrogen sulphide and sulphur dioxide were not identified in any of these experiments, although in some of the filtrates there was a loss of sulphur which is not accounted for.

Each sulphide when treated alone was dissolved rather slowly, but when two were treated together the action on one of them was greatly accelerated and that on the other retarded. Sphalerite dissolved more readily in the presence of pyrite. The acid generated by the oxidation of iron was not the only factor that favored solution, for when the iron sulphide was placed on a filter above zinc sulphide the rate of solution of zinc sulphide was not greatly increased. Gottschalk and Buehler conclude that the acceleration of the reactions is due to electric currents generated by contact of minerals of different potential. The electric current flows from the mineral having the higher potential, so the one of lower potential will dissolve more rapidly, the one of higher potential being protected from oxidation and solution.

Gottschalk and Buehler arranged several minerals in a series analogous to the electromotive series of the metals, the values having been determined by the use of the Ostwald potentiometer. The results of the experiments are shown below. The force generated while any two of these minerals are immersed in a solution tends

[1] Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides: Econ. Geology, vol. 7, pp. 15–34, 1912.

to accelerate the oxidation and dissolution of that sulphide which stands lower in the series and to retard the oxidation of the one that stands higher. It is noteworthy that the experiments were made with distilled water. The potential varies with the solution, and for some salts the relations are not those indicated in the table.

Potential, in volts, of several sulphides measured in distilled water against copper wire.

Marcasite	+0.37	Chalcocite	+0.14
Argentite	+.27	Hematite	+0.08 to .26
Cassiterite	+.27	Cuprite	+.05
Chalcopyrite	+0.18 to .30	Niccolite	+.02
Enargite	+.18 to .23	Domeykite	+.01
Molybdenite	+.20	Metallic copper	.00
Covellite	+.20	Stibnite	—0.17 to .6
Pyrite	+.18	Sphalerite	—.2 to .4
Bornite	+.17	Metallic zinc	—.83
Galena	+.15		

According to this table marcasite shows the highest electromotive force and sphalerite shows the lowest for the minerals, the difference being more than 0.6 volt. Metallic zinc shows a negative relation to copper of 0.83 volt, and there is a difference of 1.2 volts between the highest and lowest member of the series.

A piece of pyrite and a piece of galena, each 2 inches long and about 1 inch square, each having copper wire attached near one end, were placed in a small dish containing ordinary distilled water. The wire did not touch the water, nor were the minerals in contact. A circuit formed by placing a galvanometer between the free ends of the wires showed the same difference in potential that is shown in the above table and recorded a current of about 5 microamperes. In the course of a few days, the circuit being maintained, the galena became coated with lead sulphate, while a similar piece of galena, placed in the same solution but not in circuit, remained perfectly bright. The pyrite showed no evidence of oxidation.

Electric activity in ore deposits has recently been treated by R. C. Wells.[1] Nearly all the metallic mineral sulphides and oxides, except zinc blende, are good conductors of electricity. This sulphide and nearly all sulphates, carbonates, and silicates are poor conductors. Their potentials vary greatly with variations in the solutions and in the minerals employed, and as chemical activity continues the salts that are formed by the decomposition of minerals will themselves cause the electrical action to change, as is shown by changes of potential. The acid and oxidizing solutions in general gave the highest potentials and the alkaline and reducing solutions the lowest.

[1] Wells, R. C., Electric activity in ore deposits: U. S. Geol. Survey Bull. 548, 78 pp. 1914.

Large currents are seldom found in the earth, but small currents, locally generated, may have some potency. As stated by Wells, it would be incorrect to say that "the electric batteries are run down," yet we can not expect to find batteries in the field comparable in intensity to those constructed in the laboratory. In the earth there are strong tendencies toward equalization and adjustment of potentials by chemical reaction. Indeed, "zero potential" is itself the potential of the earth.

Vogt[1] pulverized 6 grams each of chalcocite, bornite, pyrrhotite, chalcopyrite, and pyrite and treated them separately in 100 cubic centimeter jars with aqueous solutions containing 30 grams of ferric chloride. After standing several years at about 14° C. they were dissolved in the order named. The filtrates from chalcocite and bornite showed a trace of sulphate, those from chalcopyrite a stronger trace, and those from pyrite a still stronger trace. Sulphur separated from the first four minerals named and probably also from pyrite. Sulphur did not appear to oxidize to sulphate in the reaction with chalcocite, though oxidation occurred in some degree with pyrite and pyrrhotite.

If the metal magnesium is placed in contact with zinc sulphate, magnesium sulphate is formed and zinc is liberated. If zinc is placed in contact with iron sulphate, iron is precipitated and zinc sulphate is formed. As a result of these and similar experiments the metals may be named in a vertical series in which any metal will displace those below it and be displaced by those above it. If in a voltaic cell the several metals are used as electrodes in dilute acid solution the strength of the current or its voltage will depend on the metals used; and thus also a vertical series of metals can be tabulated, the position of each metal in the table being determined by voltage.[2] Moreover, in this series, called the electromotive series, the metals are in the same order as in the one mentioned above. By measuring the voltage of each metal against a calomel electrode the values stated below are obtained.

This series defines the chemical activity of the free metals. Those below and including palladium are usually native; those above palladium and below hydrogen are frequently native; those above hydrogen and below zinc are very rarely native, and those above zinc and including it are never native. Those below copper do not form natural oxides, but many of those above it do.

[1] Vogt, J. H. L., Problems in the geology of ore deposits, in Pošepný, Franz, The genesis of ore deposits, pp. 676–677, 1902.

[2] Le Blanc, Max, Lehrbuch der Electrochemie, pp. 214–215, 1903. In the series as stated by Alexander Smith (Introduction to general inorganic chemistry, p. 362, 1912) copper and arsenic and also bismuth and antimony are reversed.

Electromotive potentials of metals.[1]

	Volts.
Never native:	
K	−3.2
Na	−2.8
Ba	−2.8
Sr	−2.7
Ca	−2.5
Mg	−1.5
Al	−1.2
Mn	−1.0
Zn	−0.7
Rarely native:	
Fe	−0.4
Co	−0.3
Ni	−0.2
Pb	−0.1
Sn	−0.1
H	±0.00
Frequently native:	
Sb	+0.1?
Bi	+0.2?
As	+0.3?
Cu	+0.3
Ag	+0.8
Hg	+0.8
Usually native:	
Pd	+0.8
Pt	+0.8
Au	+1.5

It should be noted that this series defines the activity of the metals only when they are free; it has no bearing on the reactions that involve double decomposition, in which a radicle in one salt replaces a radicle in another. In nature the metals above iron are not free either in primary or secondary ores, but if they were free in primary ores they would soon form salts by attack of carbonate or sulphate waters, or by displacing hydrogen in water itself.

The above table shows only the general tendencies of the groups of metals. The geologic activities of individual elements of the groups to form native metals are not all defined by their positions in the table. Gold occurs free and also in combination with tellurium and selenium in primary ores. In secondary ores it is invariably free. Platinum also is free in primary ores; in some deposits it forms also the arsenide, sperrylite. Silver, mercury, and copper are commonly secondary, much more commonly than antimony and arsenic. Some native bismuth is primary. Tin, the metal next above

[1] Abegg, R., Auerbach, F., and Luther, R., Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten: Deutsche Bunsen-Gesell. angew. physikal. Chemie, abh. 5, pp. 196–206, 1911. Values for aluminum and platinum are from Le Blanc, op. cit.

hydrogen, is almost unknown in the native state, but native copper, which is below hydrogen, is very common. In its alteration activities lead behaves much more like antimony than copper. Native tin, nickel, cobalt, and iron are so rare as to be classed as "mineral curiosities." Except tin, they are found only in meteorites and in very rare types of igneous rocks and they break down readily, forming oxides and other compounds. Native zinc has been reported, but its occurrence is doubtful.

In the table below the solubilities of several anhydrous sulphates are compared.

Anhydrous sulphates held in solution in a liter of water at 18° C.

[After Kohlrausch.]

	Grams.
$BaSO_4$	0.0023
$PbSO_4$	.041
$CaSO_4$	2.0
Ag_2SO_4	5.5
K_2SO_4	111.1
Na_2SO_4	168.3
$MgSO_4$	354.3
$ZnSO_4$	531.2

In the table below the solubilities of several hydrated sulphates are compared.[1]

Hydrated sulphates dissolved in a liter of water at about 20° C.

	Grams.
$FeSO_4.7H_2O$	264.2
$CuSO_4.5H_2O$	423.3
$Al_2(SO_4)_3.18H_2O$ (at 0°)	868.5
$MgSO_4.7H_2O$	1,160.0
$ZnSO_4.7H_2O$	1,610.0
$Na_2SO_4.10H_2O$ (at 31.25°)	4,800.0

The chemical practice in the leaching process at Rio Tinto, Spain,[2] is said to be as follows. The ore heaps are built up with open spaces to give ready access of air and water. In the presence of these the following reactions, according to Austin, take place:

$$FeS_2+7O+H_2O=FeSO_4+H_2SO_4.$$

The ferrous sulphate oxidizes to ferric sulphate thus:

$$2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O.$$

[1] Data from Comey's and from Seidell's dictionaries of solubilities. I have utilized also Lindgren's compilation, U. S. Geol. Survey Prof. Paper 43, p. 181, 1905.

[2] Austin, L. S., The metallurgy of the common metals, 2d ed., pp. 351–353, San Francisco, 1909.

The ferric sulphate reacts on chalcocite and changes it to sulphate as follows:

$$Fe_2(SO_4)_3+Cu_2S=CuSO_4+2FeSO_4+CuS.$$

This reaction is relatively rapid, and, accordingly, about half the copper goes into solution in a few months. The covellite molecule remaining is further dissolved according to the following reaction:

$$Fe_2(SO_4)_3+CuS+3O+H_2O=CuSO_4+2FeSO_4+H_2SO_4.$$

This reaction is slow, but in two years, under favorable conditions, 80 per cent of the remaining half of the copper is dissolved. These chemical processes illustrate in a large way the processes of solution of chalcocite under natural conditions.

Copper is precipitated from sulphate solution by alkaline silicates. E. C. Sullivan[1] placed finely ground materials—such as orthoclase, albite, amphibole, and clay gouge—in flasks with copper sulphate, silver sulphate, and other salts. They remained several days at room temperature, being occasionally shaken. The solutions were dilute, and the precipitation in many of the flasks was nearly complete. Whether contact was maintained for a few hours or a few months made little difference. Analyses of the filtrate before and after the reactions showed that considerable material, especially the alkalies, had been dissolved from the silicate. The filtrate from 25 grams of powdered orthoclase with 40 cubic centimeters 0.1 normal sulphuric acid gave the following results:

Orthoclase and sulphuric acid; content of 40 cubic centimeters.

Constituent.	Grams.	Millimols.
SiO_2	0.0242	.....
Al_2O_3	.0313	[a]0.92
CaO	Undet.	.....
MgO	.0010	.03
K_2O	.0556	.59
Na_2O	.0108	.17
Total	.1229	1.71
Total in 50 cubic centimeters	.1536	2.14

[a] This is the number of divalent millimols to which 0.0313 gram alumina is equivalent.

The acid has dissolved somewhat less than its own equivalent of bases from the orthoclase. No change in the concentration of the sulphate radicle could be detected.

[1] Sullivan, E. C., The interaction between minerals and water solutions, with special reference to geologic phenomena: U. S. Geol. Survey Bull. 312, pp. 37–64, 1907. Also, The chemistry of ore deposition—precipitation of copper by natural silicates: Econ. Geology, vol. 1, pp. 67–73, 1905.

Albite ($NaAlSi_3O_8$) in contact overnight with cupric sulphate solution gave the following results:

Experiment with albite and cupric sulphate.

Constituent.	Grams.	Millimols.
Copper in 50 cubic centimeters:		
Originally	0.1266	1.99
Finally	.0343	.54
Loss	.0923	1.45
Content of 38.34 cubic centimeters:		
SiO_2	.0046	.....
Al_2O_3	.0020	.06
CaO	.0107	.19
Na_2O	[a].0516	.83
Total	.0689	1.08
Content of 50 cubic centimeters	.0898	1.41

[a] Including a little MgO and K_2O.

Twenty-five grams powdered orthoclase were placed in contact for two days with 50 cubic centimeters of silver sulphate solution. The silver was almost completely precipitated.

Experiment with orthoclase and silver sulphate.

Constituent.	Grams.	Milli-equiva-lents.
Silver in 50 cubic centimeters:		
Originally	0.1066	0.98
Finally	.0039	.04
Loss	.1027	.94
Content of 30.27 cubic centimeters:		
SiO_2, Fe_2O_3, etc.	.0007	.....
CaO	.0001	.....
MgO	.0004	.02
K_2O	.0170	.36
Na_2O	.0073	.23
Total	.0255	.61
Total in 50 cubic centimeters	.0421	1.01

Experiments by Sullivan on shale from Morenci, Ariz., are described by Lindgren[1] as follows:

Fifty grams of shale finely ground in agate mortar were placed in 100 cubic centimeters of solution of cupric sulphate containing 0.0025 gram of copper per cubic centimeter. After standing for four days, with occasional shaking, the solution contained but 5 per cent of that amount of copper. A solution of the same strength had lost all its copper after four months' contact with shale. A concentrated solution with original content of 0.7645 gram copper per cubic centimeter had but 0.7058 gram copper per cubic centimeter after a few days'

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 192, 1905.

contact, 100 cubic centimeters of solution thus giving up nearly 0.6 gram copper (0.75 g. cupric oxide, CuO) to 50 grams shale.

A certain amount of acid radicle is also taken from the solution by the shale. This loss in one experiment with the dilute copper sulphate mentioned was something over 10 per cent of the total SO_4.

The shale in turn gives off a part of its constituents to the solution, about 0.2 gram having been found in 100 cubic centimeters after treatment with the dilute copper-sulphate solution. This is 0.4 per cent of the 50 grams shale taken. Of this dissolved matter, mostly present as sulphate, one-third to one-half was potassium oxide, most of the remainder being magnesium oxide and calcium oxide, with sodium oxide, manganese oxide, ferric oxide, and silica in smaller quantities.

The acidity of the solution was not increased by removal of copper, analysis showing that copper precipitated in excess of that equivalent to the acid radicle removed was replaced in solution by other bases as sulphates.

Reactions of this character are probably at some places important processes in the enrichment of ore bodies, for the essential conditions of the experiments commonly exist in nature. The neutralization of the acid solutions by the alkaline silicates permits also such reactions as are favored by a neutral environment.

In some silver and copper mines clay gouge and highly altered material carry valuable minerals. This altered material may have been produced by the attrition of rock originally metalliferous, but the experiments described above suggest processes by which it may have been enriched. The results of experiments showing the extent to which these reactions may go on when sulphides also are present are not available.

According to Stephen H. Emmens,[1] hydrogen sulphide and sulphur dioxide form with sulphur as intermediate steps in the oxidation of pyrite. These compounds, however, will oxidize where oxygen is in excess, or in the absence of water pressure they can readily escape; thus hydrogen sulphide would have but little effect in precipitating the metals in the oxidizing zone.

The statement of Emmens that hydrogen sulphide is formed in the oxidation of sulphides was made as early as 1892, but it was not supported by a record of experiments, and it has not received the attention that it probably deserves. Buehler and Gottschalk showed that pure water does not generate hydrogen sulphide in the presence of oxygen with sulphides, but it is formed on contact with some sulphides and weak sulphuric acid.

The crystallized and the freshly precipitated sulphides of a metal may show considerable difference in solubility in water, as is indicated by the table below, which gives the results of a number of determinations by Weigel,[2] who used a sensitive apparatus for measur-

[1] Emmens, S. H., The chemistry of gossan: Eng. and Min. Jour., vol. 54, pp. 582–583, 1892.

[2] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, pp. 293–300, 1907.

ing these very low solubilities. Weigel showed also that the amount of lead sulphide dissolved in water increases for a short period and then decreases, owing probably to the precipitation from the solution of crystallized galena, or some dense form which is less soluble than the freshly precipitated sulphide.

Solubility of the sulphides of the heavy metals in distilled water at 18° C.

[Mols × 10^{-6} per liter.]

Crystallized.		Freshly precipitated (probably amorphous).	
MnS	54.5	MnS	71.60
Pyrrhotite	53.6	ZnS	70.60
Pyrite (Freiberg)	48.89	FeS	70.1
Pyrite (artificial)	40.84	CoS	41.62
Wurtzite (artificial)	28.82	NiS	39.87
Millerite (artificial)	16.29	CdS	9.00
Greenockite (artificial)	8.99	Sb_2S_3	5.2
Zinc blende (Santander)	6.55	PbS	3.6
Zinc blende (artificial)	6.63	CuS	3.51
Cu_2S	3.1	As_2S_3	2.1
Galena (Freiberg)	1.21	Ag_2S	.552
Galena (artificial)	1.21	Bi_2S_3	.35
Galena (from precipitated PbS)	1.18	HgS	.054
SnS_2	1.13		
Ag_2S	.5522		
SnS (crystallized)	.14		

The reactions of sulphate solutions with sulphides were first studied by Anthon.[1] His experiments were repeated and amplified by Schuermann,[2] who established a series in which the sulphides of any one of the metals thereof will be precipitated at the expense of any sulphide lower in the series. He used 50 cubic centimeters, of about 0.1 formula weight, of solutions of the salts noted below with 100 cubic centimeters of water and introduced small amounts of metallic sulphides.

Amounts of various salts used in Schuermann's experiments.

	Grams per liter.
$CuSO_4.5H_2O$	24.880
$Pb(NO_3)_2$	33.018
$ZnSO_4.7H_2O$	28.642
$NiSO_4.7H_2O$	28.014
$Co(NO_3)_2.6H_2O$	29.014
$FeSO_4.7H_2O$	27.742
$HgCl_2$	27.054
$CdSO_4.\frac{1}{2}H_2O$	25.541

[1] Anthon, E. F., Ueber die Anwendung der auf nassem Wege dargestellen Schwefelmetalle bei der chemischen Analyse: Jour. prakt. Chemie, vol. 10, pp. 353–356, 1837.

[2] Schuermann, Ernst, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, p. 326, 1888.

	Grams per liter.
$BiO_3.H_3(NO_3)$	30.311
$MnSO_4.5H_2O$	24.042
$AgNO_3$	16.955
$SnCl_2.2H_2O$	22.406
$PdCl_2$	17.694
$\frac{1}{2}As_2O_3$	9.884
$C_4H_4O_6\frac{SbO}{K}.\frac{1}{2}H_2O$	33.119

The sulphides were placed in 150 cubic centimeter flasks that were closed with a Bunsen valve to allow steam to escape and to prevent access of air. On the application of heat the metal in solution as sulphate, as chloride, or as nitrate was precipitated as sulphide, and the metal of the introduced sulphide simultaneously went into solution. In general, the attack was continued for several hours. Schuermann's series is as follows: Palladium, quicksilver, silver, copper, bismuth, cadmium, lead, zinc, nickel, cobalt, iron, thallium, and manganese. Under the conditions named any metal in solution will, according to Schuermann, be precipitated as sulphide if in contact with the sulphide of a metal lower in the series, and the metal lower in the series will simultaneously go into solution. As a rule the reaction is the more nearly complete the farther apart the two metals are in the series.

In a series which he regards as showing the "relative affinity" of the heavy metals for sulphur, Schuermann includes antimony, arsenic, and tin. This series is palladium, mercury, silver, copper, bismuth, cadmium, antimony, tin, lead, zinc, nickel, cobalt, iron, arsenic, thallium, and manganese. Those last named have the least affinity.

Schuermann's results have been widely applied. The term "chemical affinity" is a convenient one but is used in the absence of more definite information to express a relation, not chemical constants. As pointed out by Wells, the principal results of Schuermann's experiments may be regarded as reactions establishing chemical equilibria, the salts being fixed in order of their solubilities under the conditions of the experiments. The positions of the commoner metals in the Schuermann series agree fairly well with the solubilities of the sulphides determined by Weigel, and the metals which replace those lower in the series generally have sulphides of lower solubilities than those which are replaced. As shown in the table that follows, there are, however, several discrepancies between the Schuermann series and Weigel's table.

If ammonium sulphide is added to a solution in which the metals are dissolved (in equal molar concentration) those which have the lowest solubilities are precipitated first. Under similar conditions and with equal molar concentrations the metals would be precipitated by ammonium sulphide approximately, but not exactly, in the

order indicated in the Schuermann series. This order of precipitation would hold, however, for the sulphides of the most common metals and for those which are assumed to be most important in processes of sulphide enrichment.

In the table below Schuermann's series is compared with a series showing the solubilities of the metallic sulphides as determined by Weigel, the numbers in parentheses indicating the order of (molar) solubility. In Schuermann's series the metals are arranged in the order of their decrease of "affinity for sulphur."[1] In Weigel's series the order of solubility of the freshly precipitated metallic sulphides is expressed in mols per liter;[2] to each amount stated should be applied the factor $\times 10^{-6}$.

Comparison of Schuermann's and Weigel's series.

Schuermann's series.	Weigel's series.	Mols per liter.
(1) Hg.	(1) HgS	0.054
(2) Ag.	(3) Ag_2S	.552
(3) Cu.	(4) CuS	3.51
(4) Bi.	(2) Bi_2S_3	.35
(5) Cd.	(6) CdS	9.0
(6) Pb.	(5) PbS	3.6
(7) Zn.	(10) ZnS	70.6
(8) Ni.	(7) NiS	39.81
(9) Co.	(8) CoS	41.62
(10) Fe.	(9) FeS	70.1
(11) Mn.	(11) MnS	71.6

Hydrogen sulphide is made in the chemical laboratory by treating artificial ferrous sulphide with acid. The generation of hydrogen sulphide is almost instantaneous. As recently shown by Allen, pyrrhotite is in reality a solid solution of ferrous sulphide (FeS) and sulphur. Both pyrrhotite and zinc blende dissolve in acid with noticeable evolution of hydrogen sulphide, whereas pyrite and chalcopyrite are almost insoluble in sulphuric or in hydrochloric acid. They are readily decomposed, however, in nitric, an oxidizing acid.

Several experiments were made by R. C. Wells to ascertain the rates at which hydrogen sulphide is generated by the action of cold dilute acid waters on sulphides of the metals. The ores, obtained from the Smithsonian Institution through the courtesy of Dr. J. E. Pogue, were pyrite from Leadville, Colo.; chalcopyrite from the Cactus mine, Utah; sphalerite from Webb City, Mo.; pyrrhotite from

[1] Schuermann, Ernst, Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Annalen, vol. 249, p. 326, 1888. Emmons, S. F., The secondary enrichment of ore deposits: Am. Inst. Min. Eng. Trans., vol. 30, p. 212, 1901. Weed, W. H., The enrichment of gold and silver veins: Am. Inst. Min. Eng. Trans., vol. 30, p. 428, 1901; The affinity of metals for sulphur: Eng. and Min. Jour., vol. 50, p. 484, 1890; Review of lecture by Watson Smith on Schuermann's reactions: Soc. Chem. Ind. Jour., vol. 11, pp. 869–871, 1892.

[2] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. phys. Chemie, vol. 58, p. 293, 1907.

Ely, Vt.; and galena from the Motley mine, Carterville, Mo. All these specimens appeared to be pure. They were powdered, washed with hydrochloric acid, alcohol, and ether, and sifted, the material passing a 200-mesh sieve and that held on an 80-mesh sieve being rejected. Thus the material used was free from fine dust and lumps.

In preliminary experiments the minerals were used in quantities proportional to their densities, thus insuring approximately equal surfaces. Portions of the minerals placed in flasks and covered with 0.1 normal sulphuric acid showed no visible change until a week had elapsed, when flasks containing pyrrhotite began to show a precipitate of basic ferric sulphate. No regularity was found in the variation in the acidity of the solutions on account of the simultaneous consumption and production of acid with the different minerals.

The five minerals were further exposed overnight to 0.057 normal sulphuric acid. The resulting solutions were titrated with iodine solution to ascertain the amount of hydrogen sulphide generated, the iodine solution used being, for pyrrhotite, 28.5 cubic centimeters; for sphalerite, 1.05 cubic centimeters; for galena, 0.40 cubic centimeter; for chalcopyrite, 0.29 cubic centimeter; for pyrite, 0.28 cubic centimeter.

A set of experiments exactly similar to the above was made, the resulting solutions being titrated with potassium permanganate. The consumption of the salt with the solutions from pyrrhotite greatly exceeded the consumption with those from any other mineral.

In another series of experiments the hydrogen sulphide generated by the action of cold dilute acid on pyrrhotite, on sphalerite, and on galena was determined qualitatively by lead acetate paper. There was no proof that hydrogen sulphide was formed with either pyrite or chalcopyrite, and the very small quantities indicated above (0.28 cubic centimeter for pyrite and 0.29 cubic centimeter for chalcopyrite) are not regarded by Mr. Wells as proof that hydrogen sulphide is formed by the action of acid on pyrite and chalcopyrite. The slight reduction of the iodine solution may represent a correction for the end point of the titration.

In a series of experiments by Nishihara[1] 1 gram each of various minerals that had been passed through 80-mesh screens and caught on 200-mesh screens were each treated with 30 cubic centimeters of one-eighth normal sulphuric acid. The acidity of the solutions was tested by taking 2 cubic centimeters of the solutions that had been in contact with the various minerals and titrating against tenth normal sodium carbonate. The relative reactivity of the minerals is shown on the next page.

[1] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, pp. 748–757, 1914.

Relative reactivity of minerals in decreasing acidity of eighth normal H_2SO_4.

[Results given in cubic centimeters; 2.5 indicates all acid reduced; 0 indicates no action.]

Minerals, in order of activity.	1 day.	1 week.	2 weeks.	3 weeks.	1 month.	2 months.	3 months.
Calcite	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Rhodochrosite	2.4	2.5	2.5	2.5	2.5	2.5	2.5
Siderite	.5	2.2	2.5	2.5	2.5	2.5	2.5
Nephelite	.6	1.9	2.3	2.4	2.5	2.5	2.5
Pyrrhotite	.3	1.4	1.9	2.4	2.5	2.5	2.5
Leucite	1.3	1.5	1.7	1.9	2.1	2.2	2.2
Tetrahedrite	.2	.6	.8	.9	1.0	1.1	1.4
Labradorite	.2	.2	.5	.5	.6	.9	1.2
Hornblende	.2	.2	.4	.4	.6	.7	1.1
Galena	.0	.0	.1	.1	.2	.6	1.1
Augite	.1	.2	.3	.3	.3	.8	.9
Sphalerite	.0	.0	.0	.0	.1	.2	.4
Biotite	.1	.1	.2	.2	.2	.3	.3
Fluorite	.0	.0	.0	.0	.0	.1	.2
Orthoclase	.0	.0	.1	.1	.1	.1	.2
Chalcopyrite	.0	.0	.0	.1	.1	.1	.1
Arsenopyrite	.0	.0	.0	.0	.0	.0	.1
Marcasite	.0	.0	.0	.0	.0	.0	.0
Muscovite	.0	.0	.0	.0	.0	.0	.0
Pyrite	.0	.0	.0	.0	.0	.0	.0
Quartz	.0	.0	.0	.0	.0	.0	.0

The odor of hydrogen sulphide was noted in solution with pyrrhotite, galena, and sphalerite.

To compare the relative reducing powers of minerals on ferric sulphate solution the minerals were pulverized and the powders were passed through an 80-mesh screen and caught on a 200-mesh screen, each powder being treated with 30 cubic centimeters ferric sulphate solution. The results by Nishihara are given in the table below.

Relative reactivity of minerals in reducing acidity of tenth normal ferric sulphate.

Minerals in order of activity.	1 day.	2 days.	3 days.	5 days.	7 days.
Calcite	2.9	3.0	3.0	3.0	3.0
Olivine	.6	1.0	1.5	1.9	3.0
Sodalite	1.2	1.6	2.2	2.8	2.9
Rhodochrosite	.6	.9	1.4	2.2	2.8
Siderite	.4	.6	.9	1.6	2.3
Pyrrhotite	.3	.6	.9	1.6	2.2
Leucite	.5	.7	.8	1.1	1.4
Tetrahedrite	.3	.4	.6	.8	1.3
Galena	.3	.4	.6	.7	1.0
Arsenopyrite	.1	.1	.2	.3	.5
Labradorite	.0	.0	.2	.3	.4
Sphalerite	.0	.2	.2	.3	.4
Pyrite	.0	.0	.0	.4	.4
Hornblende	.0	.1	.1	.3	.4
Enargite	.0	.0	.0	.1	.4
Marcasite	.0	.0	.1	.4	.4
Kaolinite	.1	.1	.2	.2	.3
Augite	.0	.1	.1	.2	.3
Chalcopyrite	.0	.0	.0	.2	.2
Biotite	.0	.0	.0	.0	.1
Orthoclase	.0	.0	.0	.0	.0
Muscovite	.0	.0	.0	.0	.0
Fluorite	.0	.0	.0	.0	.0
Quartz	.0	.0	.0	.0	.0

Extract titrated against tenth normal Na_2CO_3 in each test; 3=all; other figures=3 minus the cubic centimeters Na_2CO_3 used in titration.

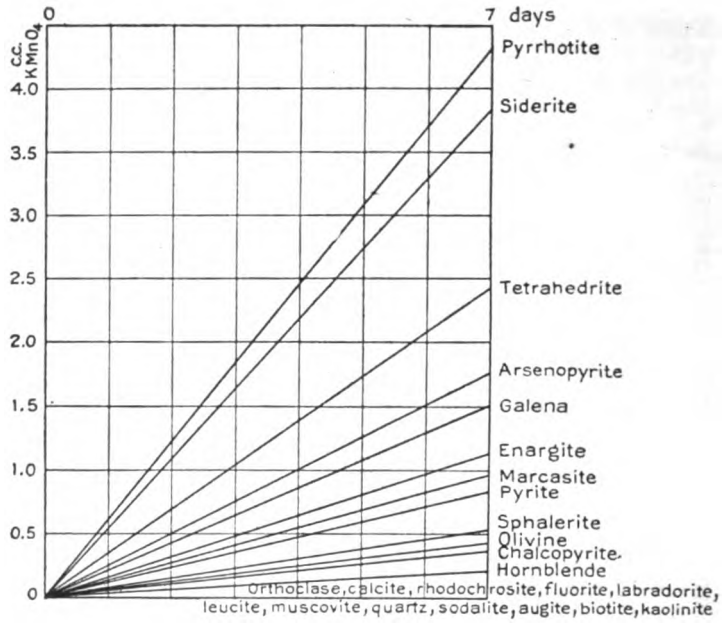


FIGURE 11.—Diagram showing relative reactivity of minerals in seven days in reducing iron in solutions of ferric sulphate. After G. S. Nishihara.

Relative reactivity of minerals in reducing acidity of tenth normal cupric sulphate and ferric sulphate.

Minerals in order of activity.	1 day.	2 days.	4 days.	8 days.	16 days.
Calcite	1.8	3.3	3.3	3.3	3.3
Siderite	.2	.5	.9	1.7	3.0
Tetrahedrite	.0	.1	.3	.7	1.4
Galena	.0	.1	.2	.6	1.1
Pyrrhotite	.0	.1	.1	.2	.7
Arsenopyrite	.1	.4	.5	.6	.6
Chalcocite	.1	.1	.1	.2	.6
Sphalerite	.1	.1	.1	.2	.6
Pyrite	.1	.1	.1	.2	.4
Marcasite	.1	.1	.1	.2	.2
Enargite	.0	.0	.0	.0	.1
Chalcopyrite	.0	.0	.0	.0	.0

Mineral, 1 gram, 80–200 mesh, each in 25 cubic centimeters tenth normal $CuSO_4$ and $Fe_2(SO_4)_3$; extract titrated against tenth normal Na_2CO_3 in each test; 3.3 equals complete reduction; 0 equals no reduction; other figures obtained by subtracting from 3.3 the cubic centimeters Na_2CO_3 used in titration. Obviously the ferric sulphate had partly hydrolyzed, yielding some sulphuric acid.

Relative reactivity of minerals in reducing iron in solution of cupric sulphate and ferric sulphate.

Minerals in order of activity.	1 day.	2 days.	4 days.	8 days.	18 days.
(Siderite)	0.2	0.3	0.6	1.5	4.2
Arsenopyrite	.2	.4	.7	1.5	2.6
Pyrrhotite	.0	.1	.4	1.0	2.5
Tetrahedrite	.0	.0	.2	.8	2.3
(Chalcocite)	.1	.1	.2	.6	1.7
Galena	.1	.1	.2	.6	1.6
Sphalerite	.0	.0	.0	.3	1.4
Pyrite	.0	.0	.0	.2	1.2
Marcasite	.0	.0	.0	.2	1.2
Chalcopyrite	.0	.0	.0	.0	.5
Calcite	.0	.0	.0	.0	.0

Mineral, 1 gram, 80–200 mesh, in 25 cubic centimeters each tenth normal $CuSO_4$ and $Fe_2(SO_4)_3$. 2 cubic centimeters extract titrated against $KMnO_4$ solution. Figures indicate the cubic centimeters $KMnO_4$ used in titration.[1]

Relative reactivity of minerals in reducing iron in ferric sulphate solution to ferrous iron.

Minerals in order of activity.	1 day.	2 days.	3 days.	5 days.	7 days.
Pyrrhotite	0.2	1.2	1.9	3.2	4.3
(Siderite)	.2	1.0	1.6	2.7	3.8
Tetrahedrite	.2	.7	1.2	1.9	2.3
Arsenopyrite	.3	.5	.6	1.2	1.7
Galena	.6	.7	1.0	1.2	1.5
Enargite	.2	.3	.5	.6	1.1
Marcasite	.2	.4	.4	.8	.9
Pyrite	.2	.3	.5	.7	.8
Sphalerite	.1	.3	.4	.....	.5
(Olivine)	.0	.2	.2	.3	.4
Chalcopyrite	.1	.2	.2	.2	.3
(Hornblende)	.0	.0	.0	.1	.2
Orthoclase	.0	.0	.0	.0	.0
Calcite	.0	.0	.0	.0	.0
Rhodochrosite	.0	.0	.0	.0	.0
Fluorite	.0	.0	.0	.0	.0
Labradorite	.0	.0	.0	.0	.0
Leucite	.0	.0	.0	.0	.0
Muscovite	.0	.0	.0	.0	.0
Quartz	.0	.0	.0	.0	.0
Sodalite	.0	.0	.0	.0	.0
Augite	.0	.0	.0	.0	.0
Biotite	.0	.0	.0	.0	.0
Kaolinite	.0	.0	.0	.0	.0

Mineral, 1 gram, 80–200 mesh, in 30 cubic centimeters tenth normal ferric sulphate. 2 cubic centimeters extract titrated against $KMnO_4$ solution. Figures show cubic centimeters $KMnO_4$ solution used in titration.[2]

F. F. Grout[3] made a series of experiments in which he placed 3 or 4 grams of minerals, each powdered to pass through a 40-mesh screen and caught on 200-mesh screens, in corked tubes with about 10 cubic centimeters of 1 per cent sodium carbonate and in similar series with other alkaline solutions. Measured amounts of the re-

[1] Nishihara, G. S., op. cit., p. 755.

[2] Idem, p. 749.

[3] Grout, F. F., On the behavior of acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 427, 1913.

sulting solutions were treated with silver sulphate in solution with a little acid. The rate at which some of the sulphides are attacked by dilute alkalies is shown below. Alkali silicates will also attack the sulphides. These figures may be interpreted as indicating the rates at which alkali sulphides form when dilute alkaline solutions react with metallic sulphides.

Order of reactivity of mineral sulphides reacting with 1 per cent solution of alkalies.

	$NaHCO_3$ 1 week at 25° C.	Same continued 1 week at 50° C.	Na_2CO_3 1 week at 25° C.	Same continued 1 week at 50° C.	K_2CO_3 1 week at 25° C.	NaOH 1 week at 25° C.
Orpiment	100	100	100	100	100	100
Stibnite	35	35	20	20	20	100
Pyrrhotite	20	25	18	20	8	10
Realgar	12	22	25	20	.....	.....
Marcasite	8	13	2	8	.....	4
Alabandite	6	14	2	10	.....	8
Pyrite	5	7	5	9	15	10
Millerite	4	8	.....	.....	.....	.....
Galena	4	9	2	8	11	10?
Blackjack	3	4	4	10	11	4
Chalcopyrite	2	3	2	8	10	.....
Stannite	2	2	.....	.....	.....	.....
Tetrahedrite	2	1	.....	.....	.....	.....
Smaltite	2	2	3	10	6	.....
Arsenopyrite	1	0?	.....	.....	.....	.....
Cinnabar	1	2	.....	.....	.....	.....
Enargite	1	1	.....	.....	.....	.....
Chalcocite	0	0	0	0	.....	.....
Bornite	0	0	.....	.....	.....	.....
Rosinjack	0	1	0	0	.....	.....
Niccolite	0	0	.....	.....	.....	.....

In the table below data from experiments of Nishihara and Grout are assembled for more convenient inspection.

Relative reactivity of minerals in contact with several solutions.

Mineral.	1 Reducing acidity H_2SO_4 2.5=all.	2 Reducing acidity $Fe_2(SO_4)_3$ 3=all.	3 Reducing Fe''' in $Fe_2(SO_4)_3$.	4 Reducing Fe''' in $Fe_2(SO_4)_3$ with $CuSO_4$.	5 Reducing acidity of $Fe_2(SO_4)_3$ and $CuSO_4$.	6 Sulphides form in 1 per cent $NaHCO_3$ solutions.
Calcite	All.	All.	.....	.....	3.3	.....
Rhodochrosite	All.	2.8	.....	.....	.....	.....
Siderite	All.	2.3	3.8	4.2	3.0	.....
Nephelite	All.	.....	.....	.....	.....	.....
Pyrrhotite	All.	2.2	4.3	2.5	.7	25.0
Olivine	.....	All.	.4	.....	.....	.....
Leucite	2.2	1.4	.0	.....	.....	.....
Sodalite	.....	2.9	.0	.....	.....	.....
Tetrahedrite	1.4	1.3	2.3	2.3	1.4	1.0
Labradorite	1.2	.4	.0	.....	.....	.....
Hornblende	1.1	.4	.2	.....	.....	.....
Galena	1.1	1.0	1.5	1.6	1.1	9.0
Augite	.9	.3	.0	.....	.....	.....
Sphalerite	.4	.4	.5	1.4	.6	1.0
Biotite	.3	.1	.0	.....	.....	.....
Fluorite	.2	None.	.0	.....	.....	.....
Orthoclase	.2	None.	.0	.....	.....	.....
Chalcopyrite	.1	.2	.3	.5	.....	3.0
Arsenopyrite	.1	.5	1.7	2.6	.6	.....
Marcasite	None.	.4	.9	1.2	.2	.....
Muscovite	None.	None.	.0	.....	.0	.....
Pyrite	None	.4	.8	1.2	.4	5.0
Quartz	None.	None.	.0	.....	.....	.....

J. D. Clark[1] treated several rocks with acid to ascertain the rate at which solutions were neutralized. Five grams of each rock, pulverized, were passed through 200-mesh screens and put in bottles with 50 centimeters tenth normal sulphuric acid and shaken daily. After 30 days the amounts of tenth normal sulphuric acid neutralized were as follows:

Neutralizing action of certain rocks on sulphuric acid.

Rock and locality.	Principal minerals in order of abundance.	Amount $N/10 H_2SO_4$ used.	Amount $N/10 H_2SO_4$ neutralized.
		Cu. cm.	*Cu. cm.*
Franciscan limestone from rear of Stanford University.	Calcite, chalcedony	50	48.5
Basalt from Stanford University quarry.	Plagioclase, augite, orthoclase, zeolites, pyrite	50	23.4
Diorite from South Fork, Trinity River, near Low Gap, Cal.	Orthoclase (sericitized), hornblende, biotite, epidote, chlorite.	50	16.7
Franciscan shale from Tesla, Cal.	Clay substance, quartz, iron-bearing minerals	50	15.1
Rhyolite from Alum Rock, San Jose, Cal.	Glass (devitrified and silicified), quartz and chalcedony, orthoclase, plagioclase, kaolin, iron stain.	50	11.0
Hornblende andesite from Marysville, Cal.	Glass, hornblende, plagioclase, orthoclase	50	11.0
Granite from Santa Lucia, Cal.	Orthoclase, plagioclase, quartz, biotite, apatite	50	4.7

R. C. Wells[2] made a series of experiments to ascertain the order of precipitating power of carbonates on metallic salts. A dilute solution containing two metallic salts in equivalent quantities was precipitated by sodium carbonate enough for one metal only. After a time the mother liquor of each experiment was analyzed and the composition of the precipitate determined by difference.

[1] Clark, J. D., A study of the enrichment of copper sulphide ores: New Mexico Univ. Bull. 75, p. 125, 1914.

[2] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911. Also U. S. Geol. Survey Bull. 609, pp. 35–36, 1915.

Summary of fractional precipitations of carbonates at ordinary temperature.

Experiment.	Quantity of mixture taken (milligram equivalents per liter).		Duration of experiment (days).	Quantity of the metal found in precipitate (milligram equivalents).	
4	8 $ZnSO_4$	8 $CaSO_4$	17	6.52 zinc	Trace of calcium.
5	20 $CdSO_4$	20 $ZnSO_4$	19	15.5 cadmium	4.5 zinc.
6	10 $FeSO_4$	10 $CaSO_4$	3	6.25 iron	Trace of calcium.
7	10 $CuSO_4$	10 $FeSO_4$	2	5.30 copper	5.35 iron.
8	8 $CuSO_4$	8 $ZnSO_4$	26	6.84 copper	0.76 zinc.
22	8 $Pb(NO_3)_2$	8 $AgNO_3$	4	8.00 lead	0.08 silver.
23	8 $Pb(NO_3)_2$	8 $Cd(NO_3)_2$	6	8.00 lead	0.42 cadmium.
24	8 $Zn(NO_3)_2$	8 $Pb(NO_3)_2$	6	7.96 lead	Trace of zinc.
25	8 $AgNO_3$	8 $HgNO_3$	24	2.28 silver	7.98 mercury.
26	8 $AgNO_3$	8 $Cd(NO_3)_2$	4	0.30 silver	7.18 cadmium.
27	8 $ZnSO_4$	8 $NiSO_4$	10	5.00 zinc	1.50 nickel.
28	8 $AgNO_3$	8 $Zn(NO_3)_2$	8	1.60 silver	3.96 zinc.
29	8 $FeSO_4$	8 $NiSO_4$	1	4.20 iron	3.06 nickel.
30	8 $FeSO_4$	8 $Zn(NO_3)_2$	1	2.66 iron	2.64 zinc.
31	8 $Cd(NO_3)_2$	8 $HgNO_3$	11	3.54 cadmium	7.36 mercury.
32	8 $MnSO_4$	8 $CaSO_4$	2	6.56 manganese	1.64 calcium.
33	8 $NiSO_4$	14.54 $MgSO_4$	5	5.94 nickel	Trace of magnesium.
34	8 $NiSO_4$	8 $MnSO_4$	9	4.04 nickel	3.80 manganese.
39	8 $AgNO_3$	8 $MnSO_4$	7	3.98 silver	5.76 manganese.
41	8 $AgNO_3$	8 $CaSO_4$	7	6.80 silver	1.56 calcium.
42	8 $CaSO_4$	8 $MgSO_4$	8	1.60 calcium	1.12 magnesium.
55	8 $HgNO_3$	8 $Pb((NO_3)_2$	6	3.50 mercury	0.75 lead.
60	8 $CuSO_4$	8 $CdSO_4$	8	7.24 copper	0.20 cadmium.
64	8 $NiSO_4$	8 $AgNO_3$	6	3.16 nickel	2.96 silver.
71	16 $ZnSO_4$	16 $MnSO_4$	18 hours.	11.96 zinc	8.96 manganese.
74	16 $MnSO_4$	16 $CaSO_4$	1 hour.	14.80 manganese	5.70 calcium.
78	8 $ZnSO_4$	8 $CdSO_4$	15	1.26 zinc	2.34 cadmium.
87	8 $NiSO_4$	8 $CaSO_4$	800	7.99 nickel	1.80 calcium.
90	20 $Fe(NO_3)_2$	20 $Pb(NO_3)_2$	1	2.40 iron	19.0 lead.
91	20 $Fe(NO_3)_2$	20 $Cu(NO_3)_2$	1	10.65 iron	10.20 copper.
92	20 $FeSO_4$	20 $CdSO_4$	1	2.90 iron	11.6 cadmium.
93	20 $ZnSO_4$	20 $FeSO_4$	1	15.80 zinc	4.2 iron.

Precipitation series deduced from the experiments on fractional precipitation of carbonates and relative precipitation of the two metals.

Experiment.	Major constituent of precipitate.	Minor constituent of precipitate.	Ratio of major to minor constituent.
55	Mercury	Lead	Large.
31	do	Cadmium	2.1
25	do	Silver	3.5
59	Lead	Copper	Large.
90	do	Iron	6.5
23	do	Cadmium	19.0
24	do	Zinc	Large.
22	do	Silver	100.0
7, 91	Copper	Iron	1.0
8	do	Zinc	9.0
60	do	Cadmium	36.0
78	Cadmium	Zinc	1.9
92	do	Iron	4.0
67	do	Nickel	2.8
26	do	Silver	25.0
28	Zinc	do	2.5
27	do	Nickel	3.3
4	do	Calcium	6.5
71	do	Manganese	1.3
93	do	Iron	3.7
7	Iron	Copper	1.0
30	do	Zinc	1.0
29	do	Nickel	1.4
6	do	Calcium	6.3
34	Nickel	Manganese	1.1
33	do	Magnesium	Large.
87	do	Calcium	Large.
64	do	Silver	1.1
39	Manganese	do	1.4
32, 74	do	Calcium	4.0
41	Silver	do	4.4
42	Calcium	Magnesium	1.4

In some of the experiments both metals were first precipitated in nearly equivalent quantities, but with lapse of time one proceeded to dissolve, the other to precipitate. The change goes on for several days at the ordinary temperature, accompanied by a gradual transformation of the precipitate from a flocculent to a more or less crystalline state. The bottles containing the solutions and precipitates were allowed to stand as long as desired, with occasional shaking, at a temperature in the laboratory of about 20° C.

The concentrations given in the table are expressed in milli-equivalents per liter, an equivalent being equal in grams to the molecular weight of the metal or radicle reduced to a univalent basis. The farther apart the metals are in the series the greater is the fractionation. The series does not represent the order of solubility of the carbonates, for some of the precipitates were basic, but it does represent the order of the precipitating power of carbonates upon metallic salts under similar conditions. The order is mercury, lead, copper, cadmium, zinc, iron, nickel, manganese, silver, calcium, magnesium. The molar solubilities of carbonates determined by Kohlrausch (see p. 492) are, in increasing order, lead, strontium, silver, barium, calcium, zinc(?), magnesium, sodium, potassium. If zinc, whose value is given as doubtful in Kohlrausch's series, is eliminated, the elements common in both series show the same order.

The following experiment was made by Nishihara:[1]

A solution of ferric sulphate and copper sulphate was brought simultaneously in contact with calcite and chalcopyrite, and the calcite precipitated iron as ferric hydroxide and copper as carbonate, and at the same time chalcopyrite was coated with the secondary bornite. When ferric sulphate was introduced the bornite coating was quickly destroyed, but later, when the calcite had neutralized ferric sulphate, the secondary deposition went on again without interruption. The calcite precipitated the iron as ferric hydroxide and copper as carbonate, as before, and at the same time reduced the acidity of the solution, and the copper sulphide was deposited as before the introduction of ferric sulphate.

In connection with this experiment the following effects on the color of pyrite and chalcopyrite were noted as the result of placing them in the hot solutions indicated:

Effect of hot solutions on colors of pyrite and chalcopyrite.

Cupric sulphate	Color unchanged.
Ferrous sulphate	Color unchanged.
Ferric sulphate	Color unchanged.

[1] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, pp. 750, 753, 1914.

Cupric and ferric sulphate.....Color unchanged.
Cupric and ferric sulphate and calcite...Color unchanged.
Cupric sulphate and calcite.....Color unchanged.
Ferrous sulphate and calcite.....Color unchanged.
Cupric sulphate and ferrous sulphate...Chalcopyrite tarnished.
Cupric, ferrous, and ferric sulphate.....Chalcopyrite tarnished, but in less degree.
Cupric, ferrous, and ferric sulphate and calcite.....Chalcopyrite tarnished.

OXIDATION, SOLUTION, AND DEPOSITION OF CERTAIN METALLIC SULPHIDES.

FACTORS CONCERNED.

In the presence of air the oxidation and the solution of the metallic sulphides take place simultaneously and it is difficult, if not impossible, to consider the two processes separately. The rate of solution depends on many factors, among them (1) the solubility of the material in water, (2) the molecular and physical structure of the material, (3) the solubility of the salts formed by oxidation, hydration, and related processes, (4) the composition, concentration, temperature, and pressure of the solutions, (5) the mineral and chemical environment, (6) the rapidity of circulation, and (7) the potential or electromotive force of the mineral compared with the electromotive force of the mineral or minerals with which it is in contact.

It is noteworthy that the natural conditions are not those which commonly exist in the laboratory, for in nature the solvent is in motion and is therefore bringing new and generally unsaturated solutions into contact with bodies that are dissolving. Thus, if sufficient time is afforded even minerals that in the laboratory are most nearly insoluble may by natural processes be completely dissolved. Even salts so insoluble as cerargyrite and anglesite may be entirely removed from the outcrops of ores.

The solubilities of the sulphates that are formed by these reactions are nevertheless important, for, other conditions being similar, it would be supposed that the metals that have the most soluble sulphates would be most readily dissolved. As shown by the table of solubilities, iron, zinc, and copper have highly soluble sulphates, whereas the solubilities of the sulphates of lead and silver are low. Although galena (p. 109) is readily attacked by cold dilute sulphate solutions, it is nevertheless slow to dissolve in metalliferous deposits. This fact—the low solubility of its sulphate—may indicate why lead lags behind iron, copper, zinc, and many other metals in its migration downward in ore deposits.

Pyrite and marcasite, which have the same formula, oxidize and dissolve at different rates, owing, probably, to a difference in their molecular structure. Cellular pyrite will oxidize more rapidly than

dense pyrite. All may ultimately become iron oxide, as illustrated by figure 12.

The importance of an oxidizing environment as a condition for the solution of some metals should be emphasized.

All the experimental evidence shows that the oxidation and solution of the sulphides in pure water is slow. Under natural conditions it may be accelerated somewhat by carbon dioxide, which is invariably dissolved in rain water and forms a weak acid that may start solution. Sulphuric acid, a more powerful solvent, is released in the presence of iron sulphides.

The recent work of Gottschalk and Buehler[1] shows that several sulphides in contact in water form weak batteries. The current flows from the mineral having the higher potential to the one having the lower potential, which is dissolved, the one with higher potential being to some extent protected from solution. These experiments should probably be interpreted as indicating particularly the relations that exist at the beginning of solution, for the electromotive force varies with variations in the solutions, which, as already stated, are continually changing. The relations considered are those which exist in the presence of free air. Under natural conditions all portions of oxidizing deposits are not equally accessible to atmospheric oxygen. Some sulphides that are readily dissolved in dilute sulphuric acid in the presence of air are practically insoluble in its absence. Chalcocite, for example, is highly stable in portions of deposits where air is excluded, but in the presence of air and acid it dissolves very readily. The solution and oxidation of the sulphides depend on so many factors that general statements can not be applied to all conditions or combinations, each mineral association presenting, in a sense, a problem in itself.

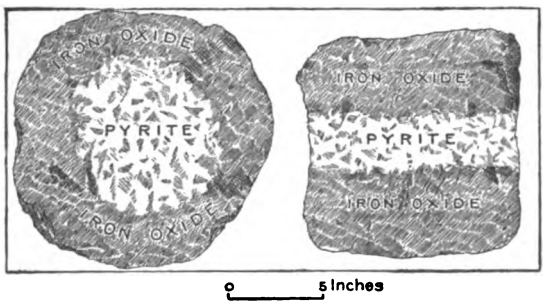


FIGURE 12.—Lumps of ore from Southern Cross and Red Lion mines, Philipsburg quadrangle, Montana, showing oxidation of pyrite. After W. H. Emmons and F. C. Calkins.

RELATIVE RATE OF SOLUTION OF SEVERAL SULPHIDES IN AN OXIDIZING ENVIRONMENT.

The following table shows the order of oxidation of some of the sulphides, according to the views of several investigators. The sul-

[1] Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides: Econ. Geology, vol. 7, p. 16, 1912.

phides that are most readily attacked are placed highest in each series. The differences that appear between certain of the series might be interpreted as indicating differences which should be expected under natural conditions, the order of oxidation depending on the environment.

Order of oxidation of sulphides, according to several authorities.

1	2	3	4	5	6
			Sphalerite.	Pyrrhotite.	Pyrrhotite.
Chalcocite.	Chalcocite.	Chalcocite.	Chalcocite.	Sphalerite.	Sphalerite.
		Bornite.	Galena.	Galena.	
	Pyrrhotite.	Pyrrhotite.	Pyrite.		
		Chalcopyrite.	Chalcopyrite.	Chalcopyrite and pyrite.	Chalcopyrite.
Pyrite.	Pyrite.	Pyrite.	Argentite.		Pyrite.

1. Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 180, 1905. At some places in Clifton district.
2. Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.: U. S. Geol. Survey Bull. 470, pp. 151–172, 1911. Above the water level.
3. Vogt, J. H. L., Problems in the geology of ore deposits, in Pošepný, Franz, The genesis of ore deposits, pp. 676–677, 1902. Order of attack of sulphides by ferric chloride.
4. Gottschalk, V. H., and Buehler, H. A., op. cit., p. 31. Table showing relative potential of several sulphides.
5. Wells, R. C. Rate of attack of 0.057 normal solution H_2SO_4 on several sulphides. (See p. 59 of Bull. 529.)
6. Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 745, 1914. Activity of minerals in decreasing acidity of eighth normal H_2SO_4 solutions.

As already stated, the relative rate of solution of the sulphides probably can not be expressed in a hard and fast series, yet certain relations hold under many, probably under most conditions. Sphalerite is so readily dissolved by acid in the absence of air that at many places it is removed even from primary ores that are in a reducing environment. Consequently in many deposits the order of the rate of solution of sphalerite, chalcocite, and pyrrhotite in acid where oxygen is in great excess can not be stated. Possibly sphalerite should be placed at the head of the series shown in the table; possibly it should be placed between pyrrhotite and chalcopyrite.

The relative rate at which chalcocite and pyrite are removed where oxygen is in excess is shown by the relations of these minerals in several deposits. Lindgren[1] notes that in the Morenci district chalcocite is often oxidized, while much pyrite remains. At Ducktown, Tenn., the "black copper" ores, composed of pyrrhotite, pyrite, and chalcocite, which have replaced the iron sulphides near the water level, quickly lose their copper content when the ores are exposed to highly oxygenated waters by the artificial depression of the level of the ground water. Solution is so rapid there that it is difficult to obtain rich chalcocite ores in mines that have been opened below the

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 180, 1905.

water level for a few years. At Ducktown, as at Morenci, chalcocite, where oxygen is present, is dissolved more rapidly than pyrite.

The pyrite in some of the leached chalcocite ore of Ducktown remains almost unaffected by the leaching, its bright crystals being distributed through a dark mass of sooty black pyrrhotite, which has been partly altered and from which practically all copper has been removed. The order of solution indicated at Ducktown is chalcocite, pyrrhotite, pyrite.

As shown by Gottschalk and Buehler, galena oxidizes more readily than pyrite. The oxidation product, lead sulphate, is so insoluble, however, that it remains to cover the crystals of galena and serves to delay further action. Galena remains in the outcrops of many sulphide ore bodies after iron and zinc compounds have been completely altered. It is said that some ore deposits in the Wisconsin zinc district were discovered by farmers who plowed up crystals of galena.

Enargite also is an exceedingly persistent mineral in outcrops. According to Reno Sales[1] it is commonly found in or near oxidized ores of the Butte copper mines, and it is said that at Tintic enargite remains in oxidized ores even after galena has been dissolved. Series 3 (table on p. 130), based on experiments of Vogt, shows the rate of attack by strong solutions of ferric chloride, an oxidizing agent, on several sulphides. Chalcocite was dissolved quickly, as it is in secondary sulphide zones, where it is exposed to solution in the presence of air. Bornite also was attacked at a relatively rapid rate. Stokes[2] showed that dilute ferric sulphate attacks chalcopyrite more readily than pyrite. All these experiments and observations seem to indicate that in the zone of oxidation in many deposits the sulphides are dissolved in the following order: Sphalerite (?), chalcocite, pyrrhotite, chalcopyrite, pyrite, galena, enargite. This series does not correspond exactly with the series of Wells (column 5 of table), which was obtained from experiments with sulphuric acid alone.

NET RESULTS OF CHEMICAL CHANGES DURING OXIDATION OF CERTAIN ORES.

The results of the chemical changes that take place during the oxidation of sulphide deposits depend largely on the minerals that form the deposits. Some gangue minerals disappear completely, others are partly dissolved, and some elements of still other minerals remain in the mass in new combinations. Not many sets of analyses of sulphide ore and of corresponding oxidized ore from the same deposit are available. The data for the deposits of Ducktown, Tenn., are fairly satisfactory. The gossans of the copper

[1] Sales, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 681, 1910.

[2] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 33, 1901.

deposits have been smelted for iron, and average analyses of thousands of tons are available from furnace records, through the courtesy of Mr. R. H. Lee and Mr. John B. Newton. Yearly averages from the smelters of sulphide ore from the same deposits are available through the courtesy of the officers of the Tennessee Copper Co. and the Ducktown Copper, Sulphur & Iron Co. On the assumption that the average of several specific-gravity determinations of the gossan (2.2) applies to the entire mass and that the average specific gravity of the sulphide ore is 4.05, the following table has been prepared to indicate the nature of the change by which primary ore becomes gossan. Column 1a shows the percentage weight of the constituents of the primary sulphide ore of the Mary mine (average of all ore smelted in 1906). Column 1b shows its percentage weight times its specific gravity (4.05) and may be regarded as expressing the number of grams in 100 cubic centimeters of the primary ore. Column 2a shows the chemical composition of the gossan (average of two large shipments). Column 2b gives its percentage weight times its specific gravity (2.2, corresponding to 39 per cent porosity). Column 3 shows the gain and the loss of the several constituents. Losses are shown for sulphur, silica, alumina, lime, iron, zinc, copper; gains for oxygen and water. Carbon dioxide and magnesia were not determined in the analyses of gossan but were almost entirely carried away.

Chemical changes by oxidation processes at Ducktown, Tenn.

	1a	1b	2a	2b	3
SiO_2	22.44	90.88	9.95	21.89	− 69
Al_2O_3	2.93	11.87	1.57	3.45	− 8.4
Fe	33.43	135.39	49.9	109.78	− 25.6
MgO	3.15	12.76	(?)	(?)	− 12.7
CaO	8.28	33.534	.35	.77	− 32.7
CO_2	2.85	11.54	.....	.....	− 11.5
S	21.23	85.98	.65	1.43	− 84.5
MnO	.44	1.78	.....	.....	.....
Cu	2.45	9.92	.86	1.89	− 8
Zn	2.79	11.30	.....	.....	− 11.3
H_2O	.....	.....	[a] 15.40	33.88	+ 33.88
O	.....	.....	[a] 21.38	47.04	+ 47.04
	99.99	404.954	100.06	220.13	−182.8

[a] H_2O and O are estimated, on the assumption that the Fe is in limonite.

Mineralogically the primary ore consists of pyrrhotite, pyrite, chalcopyrite, sphalerite, actinolite, calcite, tremolite, quartz, pyroxene, garnet, zoisite, chlorite, and micas. Small quantities of bornite, specularite, and magnetite are present and at some places graphite, titanite, and feldspars. The following is a close approximation to the mineral composition of the unoxidized ore:

Composition of primary ore at Ducktown, Tenn.

Pyrrhotite	38.5
Pyrite	5.1
Chalcopyrite	7.1
Sphalerite	4.2
Quartz	10.3
Calcite	6.0
Garnet	3.0
Amphiboles, pyroxene, zoisite, etc	25.8
	100.0

Oxidation has changed this ore into a gossan consisting essentially of limonite with a little silica and kaolin, carrying a fraction of 1 per cent of copper and sulphur.

The table below shows the results of an analysis of rich concentrates of sulphide ore from the Montana Tonopah mine, Tonopah, Nev., and an analysis of rich oxidized ore from the Valley View vein of the same district. The principal primary minerals in this district, according to Spurr,[1] are quartz, carbonates, adularia, some sericite, and sulphides of silver, antimony, copper, iron, lead, and zinc. Limonite, wad, and horn silver are deposited in the oxidized zone, with some silver bromide, silver iodide, and free gold.

Analyses of ores from Tonopah, Nev.

	1	2
Siliceous matter	15.18	16.53
Gold	.82	.62
Silver	25.92	62.54
Lead	6.21	.32
Copper	1.32	.09
Iron	9.87	1.39
Manganese	1.36	.07
Zinc	5.84	.10
Selenium	2.56	.38
Tellurium	None.	None.
Arsenic	.19	.03
Antimony	.92	.15
Magnesia	1.49	.....
Lime	3.70	.....
Carbon dioxide	6.34	.....
Sulphur	Not det.	.....
	81.72	82.22

1. Concentrates of primary sulphide ore from Montana Tonopah mine.
2. Oxidized ore from Valley View vein.

Discussing the composition of the primary and secondary ores shown by the analyses, Spurr[2] says:

Aside from the complex carbonate of lime, manganese, magnesia, and iron, the analysis of the primary sulphide ore indicates the presence of a large amount of silver sulphide—argentite. Antimonial sulphides of silver, polybasite, very

[1] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 90, 1905.
[2] Idem, pp. 92–93.

likely stephanite, and smaller amounts of galena, blende, pyrite, and chalcopyrite are also indicated. Of very great interest is the presence of a considerable amount of selenium, which occurs, in part at least, as a silver selenide, and the absence of its usually closely associated element tellurium. The chemical form of the gold is yet uncertain.

It is fair to assume that the oxidized ore in its primary sulphide state may have had a composition somewhere relatively near that of the primary sulphide analyzed. The two analyses may then be compared with the object of perceiving the changes effected by oxidation. There is no element which can be considered as having remained quantitatively unaffected during oxidation, so that merely the large relations can be glanced at. All the metals except silver and perhaps gold are present in the oxidized ore in much diminished proportions. The lead, copper, and zinc are present in small quantities. The manganese is now in the form of oxide, but very little remains; the iron is in the form of oxide, with some residual or secondary pyrite. There is much less gold in proportion to silver in the oxidized ore than in the sulphide ore; but this may be fortuitous and depend on the specimen selected. More than half the silver is in the form of sulphide, and from the very small quantity of arsenic and antimony present this portion must be nearly all in the form of argentite. The antimonial silver sulphide is very probably pyrargyrite (ruby silver), judging from microscopic observations. It is noteworthy that antimony and arsenic are present in the same proportions to one another in both analyses. There is less than a third as much selenium in the oxidized ore as in the sulphide ore, but the discrepancy is not so great as in the case of lead, copper, manganese, zinc, arsenic, and antimony; and this selenium seems to be still in the form of a silver selenide.

Therefore it is probable that during the process of oxidation the primary carbonates were attacked by surface waters and the lime and magnesia, together with most of the iron and manganese, removed in solution. Some of the iron and manganese remain as oxides. No important change in the amount of gold and silver is proved. The argentite has largely remained unaltered, but the polybasite (and stephanite if present) has probably been attacked, and much of the silver selenide. Part of this silver has been reprecipitated with little change of position as secondary argentite, not distinguishable from the primary argentite, while a large portion has been altered to chloride by the action of chlorine contained in the shallow underground waters. Most of the arsenic and antimony in the original polybasite and stephanite has been removed in solution; the rest goes to form the secondary sulphide pyrargyrite, as indicated by numerous field observations. The pyrite and the chalcopyrite have been attacked. Most of the iron in these sulphides has been removed; a small part remains as oxide, or rarely as residual or secondary pyrite. Nearly all the copper has been removed, a little remaining in the probable form of oxide.

At Cripple Creek, as noted by Lindgren and Ransome,[1] the original vein structure is destroyed by thorough oxidizing decomposition. In some sheeted lodes having many small parallel fissures and joints these openings become closed or effaced and the lode appears as a homogeneous brown, soft mass. In other places a central seam is retained and appears as a streak of soft, more or less impure kaolin; in still other places a central seam is filled with white compact

[1] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 199, 1906.

alunite, more rarely by jasperoid or opaline silica. Crusts of comb quartz, if originally present, lie included in the clayey seams, but neither the original fluorite nor the carbonates are ordinarily preserved. Very rich oxidized ore fills the central cavities of some lodes like a thick brown mud and easily flows out when the vein is opened.

Lindgren and Ransome say:[1]

> In general oxidation tends to transform sulphides, sulphosalts, and tellurides to oxygen salts and native metals, both of which may, under certain circumstances, be further changed or carried away by surface waters. The silicates in the veins are changed to a few minerals most stable under atmospheric influences—that is, kaolin, quartz, manganese dioxide, and limonite. The carbonates of the earthy metals are carried away in solution, while those of manganese and iron are changed to oxides. As waters of acid reaction, frequently containing free sulphuric acid, prevail during oxidation of vein deposits, original quartz will not be attacked. New silica, generally hydrated, may be deposited by solutions derived from the decomposition of the silicates.
>
> The processes are more difficult to follow and to establish by means of analyses than those due to primary vein formation, for it seems to be a characteristic feature of oxidation to segregate the new minerals in larger masses and thus produce a less homogeneous product; this is no doubt due to the energetic action of oxygen and of the acids set free, as well as to the increasing mobility of substance near the surface. Oxidation tends to thorough change of composition and also to obliteration of structure of the original rock or vein.
>
> Of the metallic minerals the tellurides form the most important division. The bond between the tellurium and the gold is not a strong one, and direct oxidation very easily produces residual pseudomorphs of free gold and tellurium dioxide (the mineral tellurite), which in presence of iron oxides easily changes to various tellurites such as the yellowish-green emmonsite. In the Bonanza King lode of the Midget mine occur veinlets of pyrite with tellurides. Within 30 or 40 feet of the surface oxidation has changed the tellurides to specks of native gold, while pyrite remains practically unaltered. The tellurides in fissures and joints, which form the most common mode of occurrence, will be most easily oxidized, while those occurring as metasomatic products in the rocks are not so readily reached by the surface waters.

Galena and zinc blende change to lead sulphate and zinc silicate, which may remain or even be somewhat concentrated in the altered mass. Molybdenite oxidizes very readily to yellow and blue molybdite and ilsemannite, products that do not seem to be easily carried away. Tetrahedrite yields various forms of oxidized copper compounds which, as usual, show considerable mobility. No oxidized products containing antimony have been recognized. The fluorite on exposure to oxidation loses its deep-purple color and becomes disintegrated. Eventually a part of it is dissolved in surface waters.

The following table shows the results of analyses of unoxidized ore from the Moose mine (column 1) and the oxidized portion of the same specimen (column 2). The specimens were analyzed by F. C.

[1] Lindgren, Waldemar, and Ransome, F. L., op. cit., pp. 199–200.

Knight and have been described by Richard Pearce.[1] Column 3 shows an analysis by W. F. Hillebrand of wholly oxidized ore from the 100-foot level of Stratton's Independence mine.

Analyses of fresh and oxidized ores from Cripple Creek, Colo.

	1	2	3
SiO_2	56.70	50.55	54.45
TiO_2			.80
Al_2O_3	19.35	19.93	14.45
Fe_2O_3	[a] 4.20	10.57	[a] 9.94
MnO_2		.27	[b] 1.71
CaO			1.14
MgO	.37	.12	.48
K_2O	[c] 13.97	[c] 12.13	9.96
Na_2O			.41
ZnO			[d] .53
CuO			.03
PbO			.18
Bi_2O_3			.0025
MoO_3			.008
TeO_2	.10	(TeO) .79	.19
Au	.041	.049	.52
Ag	.022	None.	.02
SO_3		2.55	.10
P_2O_5			.50
H_2O	.50	3.05	Not est.
CO_2			Trace.
S	4.75		
	100	100.00	[e] 95.4205

[a] Both Fe_2O_3 and FeO present.
[b] Both MnO_2 and MnO present.
[c] By difference.
[d] Possibly high.
[e] The difference is largely made up of combined water.

Of these analyses Lindgren and Ransome[2] say:

From the analyses and from what is known about the normal composition of unoxidized ore the following conclusions may be drawn, although it is of course realized that much more analytical work would be necessary for an exhaustive treatment of this difficult subject.

During oxidation the percentage of silica decreases moderately, probably by solution of silica set free during the decomposition of silicates. Alumina remains fairly constant, though it may locally concentrate to pure kaolin. The iron is apt to locally increase by concentration as limonite, though a part will be carried away as sulphate. Small amounts of lime and magnesia are probably leached from the rock, but the quantity is not greatly changed. Manganese is greatly concentrated, locally, on the seams of the rock. As to alkalies, the accumulation of potassium begun during the vein-forming process is continued or at least maintained during oxidation. Pyrite is converted into sulphuric acid and sulphates, and the percentage of sulphur is greatly decreased in the oxidized ore. Part of it remains as sulphate, but as there appears to have been no corresponding decrease of the bases it would seem likely that a considerable part of it was carried away as free acid. Little change is noted in the titanium, while phosphoric acid and zinc appear to have increased. The small quantities of other metals do not seem to differ notably from those observed in fresh vein material. An increase of water to 3 or 5 per cent is a

[1] Pearce, Richard, Further notes on Cripple Creek ores: Colorado Sci. Soc. Proc., vol. 5, pp. 11–16, 1896.

[2] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 202–203, 1906.

natural consequence of the formation of kaolin and other hydrated salts; locally it may increase up to 14 per cent, which is the amount contained in pure kaolin.

Silver and tellurium are removed by oxidation, but in general gold has remained. It is not easy to demonstrate whether a slight enrichment has taken place or not. Lindgren and Ransome incline to the belief that the oxidized ores as a whole are somewhat richer than the corresponding telluride ore, but this difference may depend on the original unequal distribution of the gold.

RELATIVE RATE OF SOLUTION OF SEVERAL SULPHIDES IN A REDUCING ENVIRONMENT.

When oxygen is present the process of solution is so intimately related to that of oxidation that their results can not be considered separately. The experiments of Wells on the solution of pyrrhotite, sphalerite, galena, chalcopyrite, and pyrite in dilute sulphuric acid were made in stoppered test tubes, and although no special precaution was taken to exclude atmospheric air, yet the excess of hydrogen sulphide generated in at least three of the experiments indicates a reducing environment. The minerals were attacked in the following order, determined by the amount of hydrogen sulphide generated from the three first named: Pyrrhotite, sphalerite, galena, chalcopyrite, and pyrite. This series does not agree closely with any of the others named above. Possibly the electric currents that may be generated when two of the minerals are in contact would modify the rate of solution, but it should not be supposed that the series obtained under reducing conditions in acid would be identical with the series obtained by Gottschalk and Buehler in distilled water with free access of air.

The series obtained from Wells's experiments may not apply everywhere, but geologic evidence indicates that it applies to many deposits. Thus, in the Morenci district, according to Lindgren,[1] the solutions that deposit chalcocite in the secondary sulphide zone appear not to attack pyrite as long as zinc blende is present. Pyrrhotite also is attacked more readily than pyrite in the chalcocite zone at Ducktown, Tenn. In some ore the pyrrhotite has been reduced to a powdery mass while pyrite remains fresh and untarnished.

METASOMATIC REPLACEMENT OF PRIMARY SULPHIDES BY SECONDARY SULPHIDES AND RELATIONS INDICATED BY SCHUERMANN'S SERIES.

As already stated, the series of Schuermann does not agree exactly with the solubilities of all the sulphides involved; but if compara-

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 183, 1905.

tively unimportant metals, such as arsenic, antimony, cobalt, and bismuth, are eliminated the series is almost the same as that indicated by the molar solubilities of the sulphides as determined by Weigel. The positions of zinc sulphide and iron sulphide are reversed, but according to Weigel the molar solubilities of these are almost the same. As Schuermann himself observed, the farther apart in the series any two sulphides are the more nearly complete is the replacement.

In the processes of sulphide enrichment the primary sulphides are commonly replaced pseudomorphously by the secondary sulphides. Eliminating the relatively unimportant sulphides, such as those of cadmium and bismuth, and the sulphides of arsenic and antimony, which generally enter into composition with more than one other element to make the more complex secondary minerals, Schuermann's series (and Weigel's series, except zinc sulphide) is as follows: Mercury, silver, copper, lead, zinc, iron. In the table below, for convenient inspection, the metals are placed in order of increasing solubilities of their sulphides in water, the more soluble sulphides being placed to the right of and also below the less soluble ones.

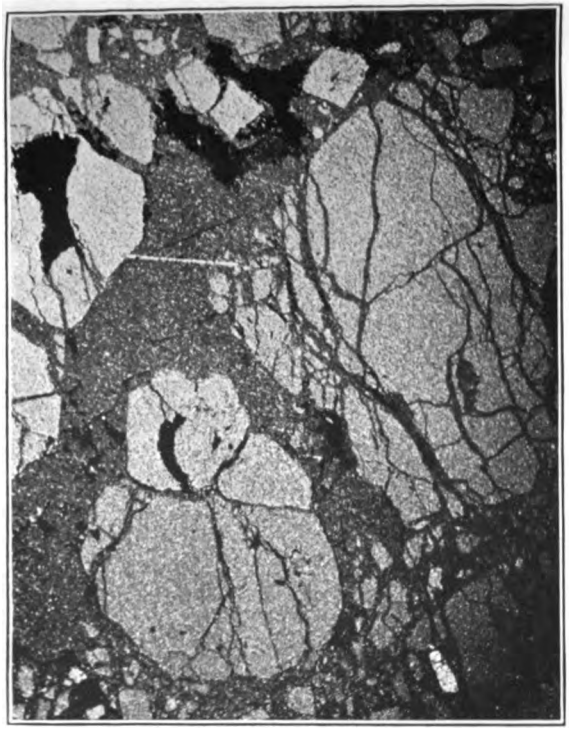
Metasomatic replacement of several sulphides.

[In the order of Schuermann's series.]

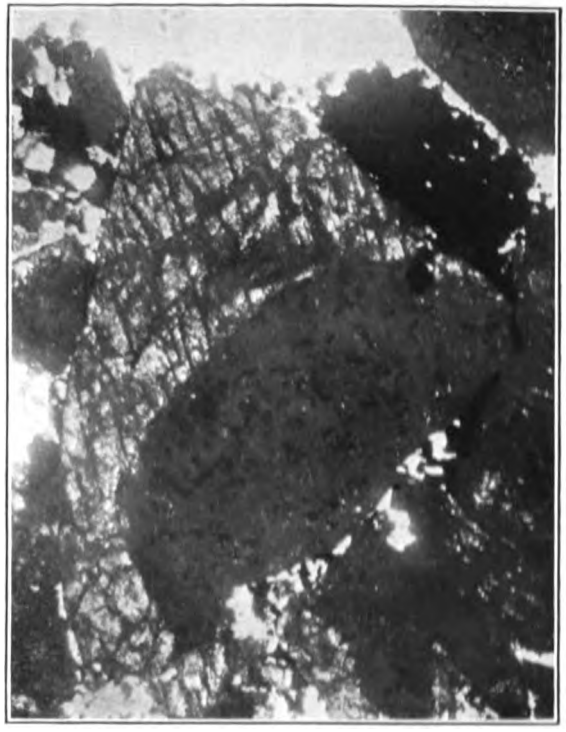
Mercury.	Silver.	Copper.	Lead.	Zinc.	Iron.
Mercury.					
Silver.		?	On PbS.	On ZnS.	On FeS_2.
Copper.			Metasomatic.	Pseudomorphic.	Pseudomorphic.
Lead.				Metasomatic.	On FeS_2.
Zinc.					"Drives out iron."
Iron.					

According to Schuermann's series it might be supposed that mercury sulphide would replace the sulphides of silver, copper, lead, zinc, and iron; that silver sulphide would replace the sulphides of copper, lead, zinc, and iron; that copper sulphide would replace the sulphides of lead, zinc, and iron; and so on.

The search for well-authenticated examples to fill in the several blocks in the table has been only partly successful. It would hardly be supposed that mercury sulphide would replace extensively the more soluble sulphides of other metals, for the solutions that transport the metals are in the main sulphate solutions, and mercury sul-



A



B

SECONDARY COPPER AND ZINC ORES.

A. Chalcocite ore from lower limit of chalcocite zone of Ryerson mine, Morenci, Ariz. Chalcocite (dark gray) is developing by replacement in pyrite (light gray). The chalcocite is accompanied by small amounts of quartz, shreds of sericite, and kaolin. Black areas are open field. After Waldemar Lindgren.

B. Zinc sulphides from Horn Silver mine, San Francisco region, Utah. The specimen in ordinary light appears to be a single mineral. With crossed nicols, as shown here, the sphalerite (isometric) appears dark, and the wurtzite (hexagonal) is light gray. After B. S. Butler.

phate has exceedingly low solubility. Moreover, mercury sulphate is easily hydrolyzed to form insoluble compounds and also tends to form the native metal and the chloride. Secondary cinnabar, although not common, is not known (p. 398).

Silver dissolves very readily in dilute sulphuric acid solutions in the presence of ferric sulphate, and at depth its sulphide is precipitated on those of lead, zinc, and iron. Carl Hintze[1] mentions pseudomorphs of argentite after proustite, stephanite, and pyrargyrite, but no examples of pseudomorphs of argentite after sphalerite, galena, or pyrite are available. The occurrences of secondary argentite are generally described as incrustations on the primary sulphides or as veinlets cutting them. Secondary chalcocite commonly contains silver, which is disseminated through and doubtless contemporaneous with the copper sulphide, but the nature of the silver mineral is uncertain. The precipitation of silver sulphide at the expense of sphalerite has been emphasized recently by Irving and Bancroft[2] in their discussion of secondary processes of enrichment of silver ores at Lake City, Colo. In view of the fact that copper sulphide is highly stable in acid solutions in the absence of an oxidizing agent it is not remarkable that the replacement of copper sulphides by silver sulphides is not common in the deeper zones.

Copper is much more abundant in its deposits than silver and the nature of its changes is more easily recognized. Long ago it was pointed out by Genth[3] that copper sulphide replaces galena in deposits at Ducktown, Tenn., and B. S. Butler found examples of covellite replacing galena in the San Francisco district, Utah. Shannon[4] described covellite replacing galena in the Caledonia mine, Coeur d'Alene, Idaho. As stated above, Lindgren has shown that copper sulphide replaces sphalerite at Morenci, and Butler found examples of the replacement of zinc sulphides by covellite in the San Francisco district. Copper sulphide replaces sphalerite at Butte, Mont., and without much doubt similar replacement is common in many mineral deposits. At Miami, Ariz.,[5] where sphalerite is rare, and in other districts where pyritic copper ore is found, pyrite is replaced directly by chalcocite without intermediate covellite. Examples of the pseudomorphous replacement of pyrite by copper sulphide are numerous, this being a common method of origin of secondary copper sulphide ores. (See Pl. IV, *A*.) Some examples are enumerated on page 186.

[1] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 442.

[2] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, pp. 64–65, 1911.

[3] Genth, F. A., Contributions to mineralogy: Am. Jour. Sci., 2d ser., vol. 33, p. 194, 1862.

[4] Shannon, E. V., Secondary enrichment in the Caledonia mine, Coeur d'Alene, Idaho: Econ. Geology, vol. 8, p. 569, 1913.

[5] Tolman, C. F., jr., and Clark, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions: Econ. Geology, vol. 9, pp. 560–594, 1914.

Although there are well-authenticated examples of sulphide enrichment of lead deposits, pseudomorphs of galena after zinc and iron sulphides are not common. According to Butler,[1] galena replaces sphalerite in the Horn Silver mine, San Francisco region, Utah. Hintze[2] notes one replacement pseudomorphous after sphalerite and one after arsenopyrite. Statements are made that lead has driven iron or zinc out of its sulphide combinations, but lode ores afford surprisingly few examples of pseudomorphous replacements of sphalerite or pyrite. Possibly the strong tendency of galena to assume its own crystal form has obscured its pseudomorphic replacement of other minerals.

It has frequently been stated that zinc sulphide has been precipitated at the expense of iron sulphide and that zinc has driven iron out of its sulphide combination, but no examples of the pseudomorphous replacement of pyrite or marcasite by zinc blende are available. On the other hand, Hintze[3] notes a pseudomorph of marcasite after zinc blende.

In even feebly acid solutions in the secondary sulphide zone a sulphide that appears to the right of the serrate line in the table on page 138 would not normally replace one to the left of the same line. Thus the copper sulphides would not be replaced by lead sulphide or by zinc sulphide, and so on. Some examples, however, do not agree with the relations indicated in this series,[4] for there are pseudomorphs of pyrite after chalcopyrite, arsenopyrite, argentite, stephanite, polybasite, ruby silver, and tetrahedrite, and pseudomorphs of marcasite after pyrrhotite, pyrite, galena, argentite, stephanite, polybasite, miargyrite, bournonite, chalcopyrite, zinc blende, and other minerals.

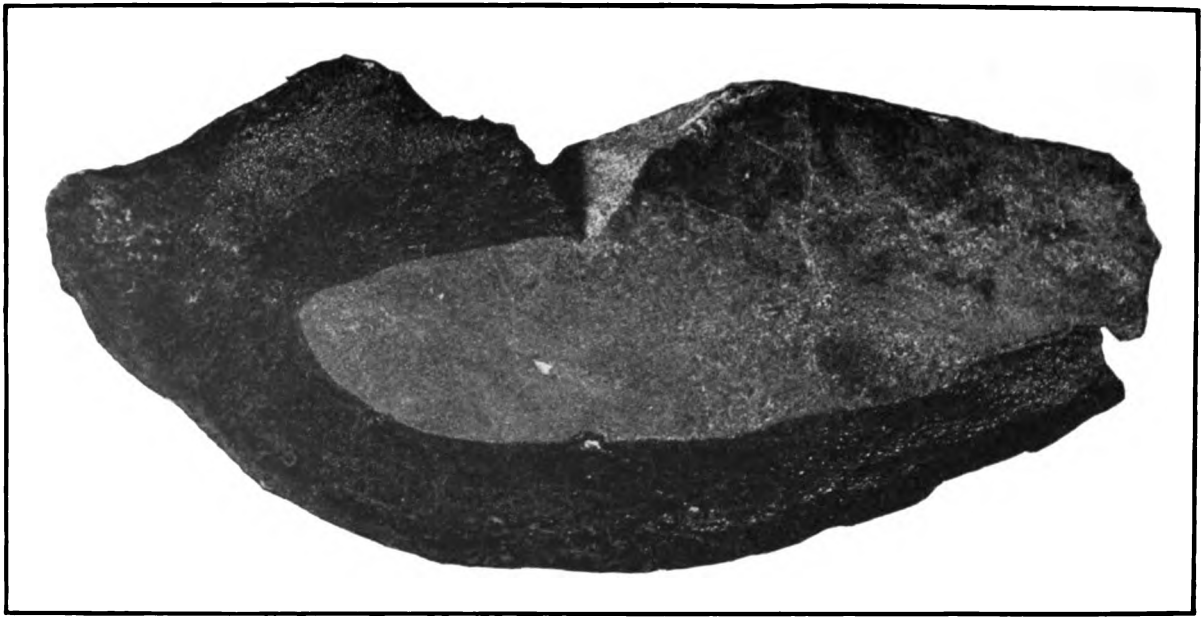
The conditions that exist where sulphide pseudomorphs are formed at the expense of a sulphide less soluble in water can not be stated. It would not be supposed that in cold acid solutions, under conditions that prevail in secondary sulphide zones, the more soluble sulphides would be fixed at the expense of the less soluble sulphides unless the metal entering into the composition of the more soluble sulphide were present in very high concentration in accordance with the well-known law of concentration effect. Probably some of the pseudomorphs mentioned above were formed in alkaline solutions and possibly some were formed at high temperatures. It should be noted, however, that the secondary replacements that are clearly of great economic significance are such as would be expected from the relations indicated by the Schuermann series.

[1] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[2] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 481.

[3] Idem, p. 820.

[4] Idem, pp. 722 and 821.



COVELLITE REPLACING ZINC SULPHIDES, FROM HORN SILVER MINE, SAN FRANCISCO REGION, UTAH.

The zinc sulphides in the center are surrounded by a zone of covellite containing considerable unreplaced zinc sulphides. After B. S. Butler.

MECHANISM OF REPLACEMENT PROCESSES IN SUPERFICIAL ENRICHMENT.

Metasomatic replacement or metasomatism is a chemical process by which a mineral or rock is replaced by another of different composition. This process goes on under widely varying conditions and operates to form epigenetic ores of every class. It has been effective in connection with the formation of some pegmatites; it is the dominant process in the formation of contact-metamorphic deposits; it is operative in forming veins at great depths and at moderate depths and near the surface; waters, magmatic or meteoric, hot or cold, form extensive ore bodies by replacement. Metasomatism is important in processes of oxidation and of sulphide deposition, and in chalcocitization it is the dominant process. In an ore body undergoing superficial alteration, replacement commonly begins along small fractures or along bedding planes, or wherever air or aqueous solutions can make their way. The result will be a mass of older ore cut by numerous planes along which younger secondary minerals are developed. But the process will go on until the secondary or later products predominate and then the original unaltered or slightly altered material tends to become a mass of nodules or rude spheres, each surrounded by secondary material. (See Pl. V.) Some minerals, particularly those that alter slowly, such as pyrite and galena, show very strong tendencies to preserve spherical shapes, for any irregularities or sharp protuberances are more likely to be attacked because they present greater surfaces to the decomposing solutions.

Metasomatism takes place by solution and reprecipitation. When a sponge of the new substance is precipitated before the old substance is completely dissolved the form of the old substance is likely to be preserved. The zone of solution and reprecipitation may be so narrow that no visible sponge is formed between the old and new substance. In the zone of oxidation the secondary substances, such as carbonates and oxides, usually contain numerous cavities or are porous or spongy, even in minute particles, though dense new crystals and crystalline bodies may form here and there in the open-textured mass. Moreover, the sponge may later become indurated by deposition of like material. At some places where a new mineral has replaced an old one metasomatically there is between the two a porous zone, or a zone occupied by a paper-thin spongy mass. One example, a nodule of zinc sulphide covered with a thick shell of copper sulphide, evidently replacing the zinc sulphide metasomatically, on being broken separated along the contact between the two minerals. Such a plane of contact, however, is not invariably a plane of separation between the old and the new substance. Another specimen, a lead ore from Creede, Colo.,[1] consisting of a

[1] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. (In preparation).

sphere of galena covered by a shell of anglesite about a quarter of an inch thick, when broken directly across the contact yielded thin plates consisting of pure lead sulphide and dense lead sulphate, with apparently a sharp contact between. When these plates were boiled in red aniline dye, some of them, on examination under the microscope, showed minute red lines representing a zone of absorbent material along which the dye had stained the specimen, the zone being clearly a very thin spongy layer surrounding the galena, itself surrounded by anglesite. The spongy zone was, however, ordinarily invisible and was so thin that it did not greatly weaken the contact. The spongy zone did not dissolve on treatment with strong acid and is doubtless anglesite, though less dense than the anglesite that surrounds it. (See fig. 24, p. 358.)

Such nodules undergoing oxidation may illustrate in a small way the rearrangement of minerals in superficial alteration. The arrangement of sheets from the outside toward the center of the nodule is in general the same as the arrangement of layers from the surface downward and is doubtless due to the same cause—a gradual depletion of the oxygen in the solutions.

The alteration of galena to anglesite involves several steps. In aqueous solutions some of the galena is dissolved as sulphide. Its solubility in water, according to Weigel, is 1.2×10^{-6} mols per liter. If air or oxidizing solution has access to the nodule through the pores of the already oxidized portion, the reaction is

$$PbS+4O=PbSO_4,$$

or, if the reaction is by ferric sulphate,

$$Fe_2(SO_4)_3+PbS+H_2O+3O=PbSO_4+2FeSO_4+H_2SO_4.$$

Lead sulphate is precipitated first as a sponge near the galena, and but a short distance from the galena this sponge is firmly cemented by new lead sulphate. In order that the reaction may continue new air or new air and ferric sulphate solutions must be supplied and some lead sulphate must go out, because volume for volume the end product carries less lead and less sulphur. There must be accession of oxygen and escape of lead and of the carrier by which the oxygen is brought to the zone of decomposition. In the zone of oxidation, which is generally the vadose zone, water is not always present, at least not in the larger openings. Drying, as well as the circulation of water, will aid in removing the oxygen-carrying solution.

Another nodule studied was of pyrite from the Southern Cross mine, near Anaconda, Mont.[1] The nodule was covered with iron oxide, which also penetrated it along fracture planes. So dense was

[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 185, 1913.

the iron oxide that no spaces were observed in it under the microscope, and it absorbed no dye on boiling, yet clearly oxygen had been passing through it and sulphur in some form escaping from it. The oxidation of pyrite to limonite, mentioned above, is supposed to involve certain subprocesses. Oxygenated waters attack iron sulphide, forming ferrous sulphate, oxygen being present outside the zone of attack. Ferrous sulphate in acid with oxygen forms ferric sulphate, which hydrolyzes and gives basic ferric sulphate, which slowly breaks down, yielding sulphuric acid and ferric hydroxide—limonite. The solid first formed—basic ferric sulphate—is slowly leached by water and doubtless after leaching becomes very permeable to water, which creeps around the film of basic ferric sulphate that lies between the pyrite and the limonite. Subsequently ferrous sulphate, passing through the film of basic ferric sulphate, may enter the outer film or concentric layer of limonite. There it is oxidized to more ferric sulphate and hydrolyzes, depositing more iron oxide on that previously formed, making it less porous. All these reactions have doubtless taken place in the ore, although it does not show even microscopic openings.

The metasomatic processes attending the deposition of primary ores and the hydrothermal alteration of rocks is fully discussed elsewhere.[1] These processes are reviewed here only as they are effective in superficial alteration and enrichment. In the zone of oxidation the openings are larger and the replacement process is more obvious. Of the material from the secondary sulphide zones which I have studied only a few specimens show a thin porous layer of material between the new and old mineral. In most of them the contact appears, even under the microscope, to be clear and fairly sharp; yet there must be openings in the outer shell large enough to let solutions of the new material pass through and to allow certain products to escape.

Chalcopyrite, according to Graton and Murdoch,[2] frequently changes to chalcocite through a zone occupied by a hairlike intergrowth of needles of covellite. Bornite also alters to chalcocite through a thin transition zone, probably covellite. Study with lenses of the highest power may show that the contact zones are less simple and less dense than they are generally supposed to be.

In most metasomatic processes, however, precipitation succeeds solution so closely that they seem to be essentially the same process. The absence of microscopically visible spaces has led to frequent statements that the new has replaced the old substance "molecule

[1] Lindgren, Waldemar, Metasomatic processes in fissure veins: Am. Inst. Min. Eng. Trans., vol. 30, p. 584, 1900. Irving, J. D., Some features of replacement ore bodies: Canadian Min. Inst. Jour., vol. 14, p. 395, 1911.

[2] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of micrographic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 43, 1914.

by molecule." This expression has not been in great favor in recent years because the theory encounters insuperable chemical difficulties. It is evident, moreover, from the figures given below, showing the sizes of openings in minerals, of microscopically visible particles, and of molecules, that in a space too small to see with the microscope there is room for myriads of molecules; the most varied reactions may occur even in a submicroscopic space.

Sizes of openings in minerals and of visible particles and molecules.

	Size in meters.
Subcapillary sheet opening (maximum)[1]	0.0000001
Particle clearly seen by microscope (minimum)[2]	.00000025
Molecule[3]	.0000000003

Only large molecules of colloidal substances are visible even in the ultramicroscope. The attraction of a molecule[3] extends through 5×10^{-8} meter. Subcapillary sheet openings are not more than twice as large, or 1×10^{-7} meter, and in such openings the combined radii of attraction of molecules would extend across the space. Water in these openings tends to attach itself permanently to solids. Microscopes of even the highest power can not make visible a body no more than twice as large as a subcapillary opening of the maximum size. In metasomatic processes, then, it is possible that material is transferred through invisible yet capillary openings. The values given above assume ordinary temperatures and pressures. At high temperatures and pressures water moves through such openings with greater freedom.

Molecules have approximately one eight-hundredth the linear dimensions of the smallest particle ordinarily made visible by a microscope. Thus, if we do not consider intermolecular spaces, more than half a billion molecules may be inclosed in a space so small that we can not see it with a microscope. Within such a space there may evidently be room for the most complicated chemical reactions, involving solution and precipitation in numerous stages, like those discussed above, all carried on in a zone so thin as to be invisible. That a zone of such permeable material may be so thin as not to weaken a contact between old and new substances is evident, for the attractions of molecules strengthening the contact might extend over a space filled by numerous other molecules undergoing change. In other words, it is possible that a thin layer, even of permeable material, may not be visible and may not greatly weaken the contact between old and new substances.

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[1] Duff, A. W., A textbook of physics, p. 115, Philadelphia, 1910.

[2] Scales, F. S., Practical microscopy, p. 168, 1909.

[3] Kaye, W. C., and Laby, T. H., Physical and chemical constants, p. 32, Longmans, Green & Co., 1911. Approximately the mean of several values given.

DEEP-SEATED METASOMATIC DEVELOPMENT OF CHALCOCITE AND COVELLITE.

In certain deposits that show the deep-seated metasomatic development of chalcocite this copper sulphide has been regarded by some as a deposit from ascending thermal waters. The phrases "upward secondary sulphide enrichment," or "ascending secondary enrichment," which have been used in discussion of the phenomena, I believe to be unfortunate. Such additions to deposits of valuable metals, together with deposits formed by the reopening and cementation of veins by ascending thermal waters, should be otherwise designated.

Metasomatism, as above noted, is a very common process in the genesis of ores. It is widely effective in the deposition of ores from ascending thermal waters and in alteration of ores by descending cold solutions, and there is nothing inherently improbable in the theory that would invoke ascending solution as an agent in the metasomatic development of rich copper sulphides. But at present the proof that it does commonly occur is meager. The best known examples are the chalcocite that rims older sulphides at Butte described by Rogers[1] and by Ray,[2] and the richer copper ores in deposits in Plumas County, Cal., where presumably chalcocitized ores are now found at moderate depths. At Butte they lie deeper, the phenomenon being observed at depths of 1,600 feet in the Leonard mine. These investigations are highly illuminating and should stimulate further study of this important problem.

Aside from the fact that these richer copper sulphides are found at unusual depths at Butte, the evidence that they were formed by ascending thermal waters at present rests largely on the fact that the rock minerals near them show little or no kaolinization or other alteration that could be due to downward-moving acid solutions. Although kaolin generally, if not invariably, does form in acid waters, it is by no means certain that all secondary chalcocite and covellite have been deposited from acid solutions. In the laboratory they may be formed more readily from pyrite in neutral solutions than in acid solutions, and the downward-moving meteoric circulation, which is acid near the surface, without doubt becomes neutral and later alkaline in depth, where it comes more and more in contact with alkaline minerals and rocks. It is true that Stokes's

[1] Rogers, A. F., Upward secondary sulphide enrichment and chalcocite formation at Butte, Mont.: Econ. Geology, vol. 8, p. 781, 1913. Turner, H. W., and Rogers, A. F., A geologic and microscopic study of a magmatic copper sulphide deposit in Plumas County, Cal., and its modification by ascending secondary enrichment: Econ. Geology, vol. 9, p. 359, 1914.

[2] Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, p. 463, 1914.

equation illustrating chalcocitization of pyrite implies the development of sulphuric acid, but this equation probably represents only one of several ways in which secondary chalcocite may be formed. Lindgren[1] states that the chalcocitization of porphyry at Morenci is generally attended by the formation of a little kaolin, although more is developed in the massive veins. According to calculations of four analyses of the altered porphyry at Morenci, only one shows the presence of kaolin.[2] In the Mount Morgan mine, Queensland, Australia (see p. 343), secondary chalcocite has formed from solutions no more acid than one that can deposit calcite. The absence of kaolin alone is not certain evidence that descending waters have not been active. (See p. 149.)

SOURCES OF THE SULPHUR OF SECONDARY SULPHIDES AND GENERATION OF HYDROGEN SULPHIDE.

The sulphuric acid solutions that carry the metals downward from the oxidized zone to a reducing environment can not be regarded as an adequate source of sulphur for the secondary sulphides. Sulphides are almost unknown in mine waters, and in the presence of air hydrogen sulphide or any dissolved metallic sulphide would be oxidized to sulphate. In only two of the 41 analyses on pages 87–89 is sulphur reported—about 1 part per million in the alkaline water of the Federal Loan mine, Nevada City, Cal. (No. 28), and in an alkaline water from Butte, Mont. (No. 2). Traces of thiosulphate, probably due to oxidation after bottling, were noted in Nevada City samples (Nos. 28, 29). Both of these were samples of alkaline solutions obtained from reducing environment.

The sulphate radicle, once formed, is exceedingly stable. It may be broken up by heat but probably not at temperatures that exist under conditions of superficial alteration. Certain bacteria break up gypsum and other stable sulphates and liberate hydrogen sulphide, but these bacteria can hardly be regarded as important agencies for the generation of hydrogen sulphide, for it is doubtful whether they could survive the presence of copper and other salts, which most of these underground mineral waters carry. It is said that carbon may reduce the sulphate radicle to sulphide, but this statement has not been confirmed experimentally. Organic material, though it has been recognized in some mine waters, is not reported in many of the samples that were taken in glass-stoppered bottles and could have little or no part in the concentration of most lode ores. The only apparent adequate source of the sulphur that combines with the

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 183, 1905.
[2] Idem, p. 169.

metals to form the secondary sulphides lies in the older sulphides. Where these sulphides are replaced pseudomorphously by secondary sulphides the sulphur has evidently remained in place, and in general the pseudomorphous replacements are attended by loss rather than by gain of sulphur.

As already stated, some of the secondary sulphide ore is found in cracks that cut the older sulphides. In some of these cracks the secondary minerals have replaced older veinlets of sulphide ore, but in others the ore has clearly been deposited in open spaces, which indicates that both the metal and the sulphur that enter into combination to form the secondary sulphide have migrated to the points of deposition. In some districts even secondary chalcocite is known to form veinlets in the older sulphide ore, one of the best examples being afforded by deposits of the Virgilina district, North Carolina, reviewed on page 248. These relations, indicating a transfer of sulphur in some unoxidized form, together with experimental evidence showing that dilute acid in contact with several primary sulphides will generate hydrogen sulphide, strongly suggest hydrogen sulphide or alkaline sulphides as agents precipitating some secondary sulphides. In view of the fact that sulphur compounds other than sulphates are practically unknown in mine waters, this conclusion might be questioned, but it should be recalled that of the samples available all but two were taken in the presence of air and that these two and many others contain ferric sulphate, which readily decomposes hydrogen sulphide. Hydrogen sulphide is used up in many ways, so it is not surprising that it does not accumulate in the upper zones of alteration.

PROCESSES OF SULPHIDE ENRICHMENT COMPARED WITH THE PROCESSES EMPLOYED FOR SEPARATING THE METALS IN QUALITATIVE CHEMICAL ANALYSIS.

Although it has not been shown that hydrogen sulphide is actually generated by bringing acid into contact with pyrite or chalcopyrite at low temperatures, or that it is an intermediate product in processes of metasomatic replacement, yet Wells's experiments for producing hydrogen sulphide (p. 119) clearly indicate the power of various sulphides to reduce natural solutions or to precipitate sulphides from soluble salts. Without doubt the same laws of chemical equilibrium apply to both processes, for the mineral that evolves hydrogen sulphide most easily will precipitate a secondary metallic sulphide most readily and will reduce acid solutions of reducible salts most readily.

The method commonly employed in qualitative analysis for separating the metals is as follows: The solution of the metals is made

acid with hydrochloric acid, which precipitates silver, lead, and univalent mercury as chlorides. Hydrogen sulphide is passed into the acid solution and precipitates sulphides of lead, bismuth, copper, arsenic, antimony, tin, and bivalent mercury. The filtrate is made alkaline, generally with ammonium hydroxide, and then ammonium sulphide is added, which precipitates the sulphides of iron, manganese, nickel, cobalt, and zinc, also aluminum hydroxide. A review of this procedure will throw light on some of the natural processes of alteration and sulphide enrichment, for in separating the metals the chemist has followed closely a natural process. In the laboratory, however, the separation is more nearly complete because the conditions as to concentration are easily controlled. Mine waters in the oxidized zone—the zone of solution—are acid and generally contain some chlorides. Silver chloride (cerargyrite), mercurous chloride (calomel), or lead chloride or chlorophosphate (pyromorphite) may be fixed in the oxidized zones of deposits carrying the metals indicated, but as chlorides are in general not abundant in mine waters, and as the chlorides named above are themselves somewhat soluble, some of the silver, lead, or mercury may be carried downward by the sulphuric acid solutions. Hydrogen sulphide, which, as already stated, is generated by the action of dilute sulphuric acid waters on certain sulphides, will precipitate from acid solutions arsenic, antimony, tin, bismuth, copper, cadmium, mercury, lead, silver, and gold. These metals may therefore be precipitated as sulphides before the solution has become less acid. Thus the sulphides of copper, lead, and silver, for example, may be formed at or near the water level, or, if the water level lies deep, in the upper part of the zone of reduction. As the solutions descend they become neutral and ultimately alkaline. When the solutions have lost acidity, sulphides of zinc, iron, nickel, and some other metals may be precipitated.

The analogy of the process of separation employed in qualitative analysis is not complete, however, for sulphide enrichment takes place in moving solutions and in solutions probably more dilute; the changes from acid solutions to neutral or alkaline solutions are gradual, especially in deposits not containing minerals that react readily with the solutions, like soluble carbonates and pyrrhotite.

Another relation should be emphasized: Although zinc sulphide is not precipitated by hydrogen sulphide in the moderately acid solution used in the laboratory, it is precipitated in solutions of very feeble acidity. Thus zinc sulphide may be precipitated from a solution of acetic acid. Iron sulphide is less readily precipitated in acid than zinc sulphide. There is not much geologic evidence that either iron or zinc is precipitated extensively from cold descending sulphuric

acid solutions which traverse lode ores in igneous or other noncalcareous rocks. In such rocks the descending waters probably remain acid to moderately great depths, for the acid waters do not react on silicates so rapidly as on calcium carbonate. These conditions would delay the deposition of secondary iron and zinc sulphides. There is some evidence that secondary chalcopyrite, pyrite, and sphalerite are formed in small cracks in the lower parts of some secondary sulphide zones, but they are surely subordinate to secondary copper sulphides in most deposits in noncalcareous rocks.

DECREASE OF ACIDITY OF DESCENDING SULPHATE WATERS.

In the discussion of the composition of mine waters of sulphide ore deposits it was stated that the waters of the shallow zones are generally acid waters. The compounds generally present near the surface are sulphuric acid, ferric sulphate, and cupric sulphate, all of which give acid reactions. Probably all these salts decrease in quantity with increase in depth or disappear. There is indisputable evidence that the total acidity of solutions decreases with depth, ferric sulphate being reduced to ferrous sulphate, which does not give an acid reaction. The accumulation of the sulphates of zinc, ferrous iron, magnesium, and calcium at great depths utilizes the sulphuric acid to make neutral salts. All these compounds are either neutral or slightly alkaline. Carbonic acid is only weakly acid and unites with bases to form alkaline carbonates, particularly those of potassium, sodium, and calcium. Alkali hydroxides and silicates also give alkaline reactions. Analyses of two samples of water taken from a column of water in the Callaway shaft at Ducktown, Tenn., indicate a decrease in acidity of more than 50 per cent within a vertical distance downward of 37 feet. Some analyses from the Capote mine, of Cananea, Mexico, show also a neutralization of acid at comparatively shallow depths. At least ten other samples, all except two taken at considerable depths, are alkaline. The conclusion is fully warranted, therefore, that acid solutions descending through sulphide ores decrease in acidity where oxygen is excluded; later they become neutral, and ultimately alkaline. The geologic data are completely in harmony with this conclusion, for there is abundant evidence that descending acid waters attack alkaline or alkaline earth silicates and alkaline earth carbonates; acid reacting with feldspars or sericite forms kaolin, and these reactions are attended by the solution of alkalies or alkaline earths as sulphates. Where limestone is attacked decrease in acidity may be attended by precipitation of gypsum.

There are reversals of these processes, it is true, for according to Stokes, the precipitation of chalcocite is attended by the liberation of sulphuric acid. This acid, however, would soon be neutralized by reactions on silicates and carbonates and could not accumulate permanently. That it is so neutralized is indicated by the common association of secondary copper ore with kaolin or gypsum.

CHANGES IN THE STATE OF OXIDATION OF DESCENDING SULPHATE SOLUTIONS.

The acidity of descending sulphate waters decreases below a certain depth, and because air is excluded the state of oxidation of the solutions likewise decreases. The degree of oxidation of iron, which is generally abundant in mine waters, affords a useful index to the state of oxidation of the solutions. The waters that pass downward from the oxidizing zone carry iron mainly in the ferric state. They may carry also some dissolved oxygen, but not much, for, according to Winkler,[1] at atmospheric pressure and at 16.87° a liter of water can dissolve but 6.84 cubic centimeters of oxygen. Underground waters are, moreover, seldom saturated with oxygen.

Dilute sulphuric acid, which reacts on certain sulphides of iron, zinc, and lead, will release hydrogen sulphide, which is available (1) for reduction of the oxygen in the water, (2) for reduction of ferric to ferrous sulphate, or (3) for the precipitation of copper or other metals which may be held in sulphate solution.

The reduction of the oxygen in the water will take place before the copper sulphide is precipitated, as oxygen tends to inhibit the precipitation of copper sulphide. It is probable also that the oxygen of the solution is reduced before ferric sulphate is attacked, although both reactions may go on together. Assuming the presence of H_2S, we may state the reactions as follows:

(1) $H_2S+O=H_2O+S.$

(2) $Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S.$

(3) $\begin{cases} H_2S+CuSO_4=CuS+H_2SO_4. \\ CuS+CuSO_4+H_2S=Cu_2S+H_2SO_4+S. \end{cases}$

If oxygen is present the reaction may go on as indicated by (1); if ferric sulphate is present, equation (2) would be possible; with neither oxygen nor ferric sulphate in the solution, equations (3) are possible.

RATE AT WHICH HYDROGEN SULPHIDE IS GENERATED FROM SEVERAL PRIMARY SULPHIDES BY COLD DILUTE SULPHURIC ACID WATERS.

As shown by experiments made by R. C. Wells (p. 119), cold dilute sulphuric acid solutions attack several metallic sulphides and

[1] Hempel, Walther, Gasanalytische Methoden, pp. 129–130, 1900.

generate hydrogen sulphide. With equal surfaces exposed, such solutions in these experiments set hydrogen sulphide free at least four times as rapidly from zinc blende as from pyrite or chalcopyrite, and about 25 times as rapidly from pyrrhotite as from zinc blende. With pyrite and chalcopyrite the amount of hydrogen sulphide generated is small and the quantities determined may represent the end points of titration, for hydrogen sulphide was not identified as a product of the reaction. Doubtless sphalerite containing considerable iron sulphide will react more readily with acid than pure zinc sulphide. The quantity of hydrogen sulphide generated with galena, sphalerite, and pyrrhotite was sufficiently great to give the results a quantitative value.

These experiments were carried on with pure minerals that had been carefully examined. Minerals so pure are seldom found in large bodies of sulphide ores, where the sulphides generally occur in more or less intimate association. Gottschalk and Buehler have recently shown that in such mixtures weak batteries are formed and that the oxidation and solution of the mineral with the lowest potential will be increased while the solution of the mineral which is higher in the series will be retarded. There is no reason to suppose that the order of solution in an oxidizing environment like that in which the experiments of Gottschalk and Buehler were carried on would correspond closely to the order of attack in a reducing environment like that which existed under the conditions of Mr. Wells's experiments. Yet the associations of the sulphides may affect the rate of their solution in the reducing zone also. Consequently the rate of attack of sulphuric acid solutions on some sulphide ores in the reducing zone can not be accurately stated. Possibly each association is a problem in itself. Where one of the metallic sulphides greatly predominates, however, it should not be supposed that a high potential would greatly retard its attack by acid in the reducing environment which is assumed to exist where the secondary sulphides are precipitated.

The laboratory experiments and geologic observations indicate that pyrrhotite is attacked very readily by acid solutions, at least where it constitutes a considerable part of the ore. The reaction with sphalerite was less rapid than with pyrrhotite but more rapid than with pyrite and chalcopyrite. Here, too, field observations support the conclusions based on the laboratory experiments available. Describing the chalcocitization of sphalerite at Morenci, Lindgren[1] notes that pyrite apparently does not precipitate Cu_2S or CuS while zinc blende is present. Weed notes also that sphalerite is present in some of the primary ores at Butte, but that it is absent in the

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 188, 1905.

enriched chalcocite ores.[1] The latter, however, contain pyrite. In a recent paper by Irving and Bancroft[2] on the deposits of Lake City, Colo., the precipitation of secondary minerals on sphalerite from downward-moving sulphate solutions is emphasized.

The data available seem therefore to indicate that in a large number of deposits at least the action of dilute sulphuric acid in the absence of air on the following sulphides is probably in the same order as that indicated by the experiments of Wells—(1) pyrrhotite, (2) zinc blende, (3) pyrite and chalcopyrite.

COMPOSITION OF THE PRIMARY ORE AS A FACTOR DETERMINING THE VERTICAL EXTENT OF THE SECONDARY SULPHIDE ZONE.

S. F. Emmons and others have emphasized the fact that the vertical extent of the secondary sulphide zone depends principally on the amount of fracturing of the primary ore body and the size, continuity, and character of the fractures. The course of such fractures determines the course of descending waters and the size, character, and continuity of open spaces control the rates at which the solutions descend.

In their descent the metal-bearing solutions react on the walls of the watercourses, and these reactions produce changes of chemical equilibria and deposition of certain metals. These changes depend not only on the rate at which the solutions descend but also on the chemical environment through which they pass. In limestone or in calcite gangue the downward migration of copper would be delayed at least temporarily by the formation of carbonates (see p. 311) and calcite would quickly drive gold from acid solutions in which it was held dissolved as chloride.

As already stated, dilute acid waters dissolve pyrrhotite more rapidly than sphalerite and sphalerite more rapidly than pyrite and chalcopyrite. The action on pyrrhotite and sphalerite is attended by the liberation of hydrogen sulphide, which precipitates several of the metals in acid solution. Under similar conditions, because the reactions are brought near to completion more quickly, the vertical extent of the zones of secondary ores should be less in primary ores which carry abundant pyrrhotite than in ores of pyrite and chalcopyrite which contain no pyrrhotite, and although such secondary zones might be richer they would not extend so deep.

The attack of acid solutions on sphalerite is less vigorous than on pyrrhotite but more vigorous than the action on pyrite and chalcopyrite; consequently deposits that carry sphalerite should

[1] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 78, 1912.

[2] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, pp. 64–65, 1911.

have secondary zones which are not so extensive vertically as those of deposits that contain pyrite and chalcopyrite with neither sphalerite nor pyrrhotite. Briefly stated, the vertical extent of the secondary sulphide zones should vary inversely with the rate at which the descending solutions attack their primary minerals.

Principal mineral combinations of three groups of copper deposits.

1	2	3
Pyrrhotite ores with pyrite and chalcopyrite, with or without zinc blende.	Pyritic ore with sphalerite and chalcopyrite, and with little or no pyrrhotite.	Pyritic chalcopyrite ores, with little or no pyrrhotite or zinc blende.
Ducktown, Tenn. Gossan lead, Va. and N. C. Ely, Vt. Santiago de Cuba. Encampment, Wyo. Grants Pass, Oreg. Bingham, Utah (in part). Sudbury, Ontario.	Morenci, Ariz. Santa Rita, N. Mex. (in part). Shasta County, Cal. Velardeña, Mexico. Jerome, Ariz. Cananea, Mexico (in part).	Butte, Mont. (in part). Bisbee, Ariz. Globe, Ariz. Miami, Ariz. Ray, Ariz.

In the foregoing table certain deposits have been so grouped that three classes of copper ores may be inspected to ascertain whether the secondary chalcocite zones have a greater vertical extent in pyrrhotite deposits, in sphaleritic deposits, or in copper deposits that contain little or no sphalerite or pyrrhotite. Those in the first column contain considerable pyrrhotite; all of them are known to have comparatively shallow chalcocite zones; in general the lower limit of chalcocite is from 50 to 250 feet below the present surface. Some of these deposits are known to be comparatively tight and relatively impervious to the downward migration of mineral waters; consequently they may not afford examples ideal for comparison. Nevertheless I can find no example of a deposit that carries abundant pyrrhotite in which secondary sulphides are shown to have been deposited at great depths.

On comparing the deposits of column 1 with those of column 3 it is clearly apparent that the chalcocite zones in the latter are of much greater vertical extent; indeed, they include the deepest chalcocite zones that have been developed. In several of the deposits of column 3 chalcocite extends to depths ranging from 1,000 to nearly 1,500 feet below the surface. It is found at still greater depths at Butte, Mont., but an increasing trend of opinion held by those most familiar with these deposits indicates that the chalcocite of the lower levels of the Butte mines is primary. In some of the deposits of Arizona the secondary zones are very extensive vertically, owing to the great distance to the zone of saturation. Undoubtedly some of the deposits of column 3 are more highly fractured than some of those of column 1, consequently these examples are likewise not ideal for comparison. Yet the fact that none of the deposits with

deep chalcocite are known to carry appreciable pyrrhotite appears to be significant.

The deposits of column 2 have chalcocite zones which in general are of greater vertical extent than those of column 1 and less than those of column 3, but possibly the differences are too slight to give the figures much significance. It is a fact familiar to all, however, that rich silver ores commonly give way in depth to primary ores containing abundant sphalerite, the transition zone being at some places comparatively thin.

From the comparison of the several groups of deposits investigated, it is concluded that with approximately similar temperatures, rainfall, erosion, head, permeability, and other conditions, the vertical extent of the secondary sulphide zone depends on the mineral composition of the primary ore. In general, ores containing abundant pyrrhotite are not enriched to depths so great as those containing pyrite and chalcopyrite but little or no pyrrhotite. The influence of zinc blende can not yet be positively stated.

The influence of the mineral composition of the primary ores on the vertical extent of the secondary zones is not so simple as may be inferred from the illustration noted above. This subject is treated separately for each of the more important metals on pages that follow.

COPPER.

PRINCIPAL COPPER MINERALS.

The names and the chemical composition of the principal copper minerals are given below:

Copper	Cu.
Chalcanthite	$CuSO_4.5H_2O$.
Pisanite	$(Cu,Fe)SO_4.7H_2O$.
Brochantite	$Cu_4SO_4(OH)_6$ or $4CuO.SO_3.3H_2O$.
Nantokite	$CuCl$.
Atacamite	$Cu_2Cl(OH)_3$ or $CuCl_2.3Cu(OH)_2$.
Malachite	$Cu_2(OH)_2CO_3$ or $2CuO.CO_2.H_2O$.
Azurite	$Cu_3(OH)_2(CO_3)_2$ or $3CuO.2CO_2.H_2O$.
Chrysocolla	$CuSiO_3.2H_2O$ or $CuO.SiO_2.2H_2O$.
Dioptase	CuH_2SiO_4 or $CuO.SiO_2.H_2O$.
Turquoise	$Cu_2O.Al_2O_3.2P_2O_5.9H_2O$ (?).
Cuprite	Cu_2O.
Tenorite	CuO.
Copper pitch ore.[1]	
Chalcocite	Cu_2S.
Covellite	CuS.
Bornite[2]	Cu_5FeS_4.

[1] A complex hydrated oxide.

[2] Formula as established by B. J. Harrington (Am. Jour. Sci., 4th ser., vol. 16, p. 151, 1903). The older, commonly accepted formula is Cu_3FeS_3, also written $Cu_2S.CuS.FeS$, or $3Cu_2S.Fe_2S_3$.

Chalcopyrite	$CuFeS_2$ or $Cu_2S.Fe_2S_3$.
Enargite	Cu_3AsS_4 or $3Cu_2S.As_2S_5$.
Tetrahedrite	$Cu_3Sb_2S_7$ or $4Cu_2S.Sb_2S_3$.
Tennantite	$Cu_3As_2S_7$ or $4Cu_2S.As_2S_3$.
Famatinite	Cu_3SbS_4 or $3Cu_2S.Sb_2S_5$.

SOLUBILITIES OF SOME COPPER COMPOUNDS.[1]

At 20° C. a liter of water dissolves 172 grams cupric sulphate.[2] At 20° C. a liter of water dissolves 435 grams cupric chloride. At 15° to 16° C. a liter of water containing 16.66 grams hydrochloric acid dissolves 61.59 grams cuprous chloride.

According to J. L. Lassaigne,[3] one part of the carbonate dissolved in 3,333 parts water saturated with carbon dioxide at 10° C. at a pressure of 755 millimeters. E. E. Free[4] showed that the solubility of copper carbonate in carbonate solutions is very small.

NATURE AND RELATIONS OF THE COPPER MINERALS.

Copper, silver, and gold belong chemically to the same family. The three elements occupy exclusively the right side of the second column of the table of the periodic system and are somewhat closely affiliated. They stand apart as metals in the concentration of which the processes of sulphide enrichment are most clearly expressed. They are dissolved more or less readily in an oxidizing sulphate or chloride environment and are readily precipitated from acid waters by reactions in the sulphide environment where oxygen is excluded.

The mineral waters in the oxidizing zones of sulphide deposits contain sulphuric acid and ferric sulphate. In the presence of oxygen such solutions dissolve copper sulphide very readily, and in contact with copper compounds such a system will contain also copper sulphate. The copper sulphate in solution reacts with carbonates or with acid carbonate in solution, precipitating copper carbonate. If chlorides are abundant, copper chlorides may form. Cupric chloride is readily soluble in water; cuprous chloride oxidizes to form oxychloride. In moist countries both chlorides are unstable. In arid countries some copper chloride may accumulate as atacamite. The sulphates chalcanthite and brochantite also may be precipitated, and the basic sulphate brochantite once formed is fairly stable. The silicates of copper are probably formed by solutions bearing copper and silicic acid, which, as shown by analyses, are common in mine waters. Reactions with calcite or other alkali minerals would aid

[1] Seidell, Atherton, Solubilities of inorganic and organic substances, D. Van Nostrand Co., New York, 1907.

[2] For the solubility of hydrated copper sulphate see p. 113.

[3] Lassaigne, J. L., Jour. prakt. Chemie, vol. 44, p. 247, 1848.

[4] Free, E. E., The solubility of precipitated basic copper carbonate in solution of carbon dioxide: Am. Chem. Soc. Jour., vol. 30, p. 1366, 1908.

precipitation. Cuprite and tenorite are formed by the oxidation of various copper compounds, and native copper may be formed by their reduction. Such changes may be pseudomorphic after an older mineral. All the copper minerals mentioned above are formed in the main in the oxidized zone, and in sulphide ores none of them form in depth by deposition from hot ascending alkaline solutions.

Below the actively oxidizing zone, where air is excluded, copper is precipitated as sulphides; chalcocite, covellite, bornite, chalcopyrite, and some of the more complex compounds of antimony and arsenic are formed by these processes. Precipitation may be brought about by chemical interchange with pyrite, chalcopyrite, pyrrhotite, zinc blende, galena, and some other sulphides mainly by metasomatic replacement. The copper sulphides are precipitated also by hydrogen sulphide, which is generated by attack of sulphuric acid solutions on several of these sulphides. At ordinary temperatures only 3.51×10^{-6} mols of copper sulphide dissolves in a liter of water. In the reducing environment the copper sulphides are stable. They are insoluble even in hot solutions of concentrated sulphuric acid if a slight trace of hydrogen sulphide is present.[1]

Iron sulphide dissolves in acid, however, and it should not be supposed that the double sulphides of iron and copper would be precipitated from acid solutions which contained much copper.[2] But as the solutions descend they lose acidity, and copper sulphide is precipitated at the expense of iron sulphide, the iron going into solution. A decrease in acidity, a decrease in copper, and an increase of iron in solution bring about a state of equilibrium which is increasingly favorable to the precipitation of double sulphides, such as chalcopyrite and bornite.

The fact that the iron-bearing copper sulphides are generally precipitated in the zone below the zone of active chalcocitization is supported also by observation. Some polished sections show that pyrite has first been converted to chalcopyrite, the chalcopyrite to bornite, the bornite to covellite, and covellite to chalcocite. This phenomenon has been observed by Krusch,[3] by Graton and Murdoch,[4] by Ransome,[5] and others. In some ore from the Queen mine, near Superior, Ariz., the series, according to Ransome, is pyrite to chalcopyrite to bornite to chalcocite. A. C. Spencer[6] regards transitional

[1] Allen, E. T., oral communication.

[2] Wells, R. C., The fractional precipitation of sulphides: Econ. Geology, vol. 5, pp. 12–13, 1910.

[3] Krusch, P., Primäre und sekundäre Erze unter besonderer Berücksichtigung der "gel" und der "schwermetallreichen" Erze: Cong géol. internat., 12th session, Toronto, Canada, Compt. rend., p. 281, 1914.

[4] Graton, Joseph, and Murdoch, L. C., The sulphides of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 40, 1914.

[5] Ransome, F. L., Copper deposits near Superior, Ariz.: U. S. Geol. Survey Bull. 540, p. 147, 1914, particularly fig. 15.

[6] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 638, 1913.

changes as normal processes of chalcocitization of chalcopyrite at Ely, Nev. It is noteworthy here that normal erosion of a deposit undergoing chalcocitization will carry the chalcocite zone lower and lower, and that as it progresses downward it will be superimposed on any zone of secondary chalcopyrite or bornite that is below. It is probable that a large part of the copper from downward-moving copper sulphate solutions is precipitated as a copper sulphide directly, and that the secondary copper-iron sulphides form only after the solution has become poor in copper and relatively high in iron. This condition, as stated above, is more favorable to the precipitation of the double sulphide. From a solution rich in copper and poor in iron only the less soluble copper sulphide should be deposited. Clark states that native sulphur also will precipitate copper sulphide from copper sulphate solutions.[1]

In the oxidizing zone copper is much more soluble than gold, and, unlike gold, it may be dissolved in the absence of chlorides in sulphate solutions. Thus many deposits which contain both copper and gold show a distinct segregation of gold near the surface, whereas copper ores with subordinate gold are found in depth. The Highland Boy mine, at Bingham, Utah; the United Verde mine, at Jerome, Ariz.; and the Mount Morgan mine, in Australia, were operated first as gold mines and subsequently developed large bodies of copper-gold ores. In two of these mines the gold has probably not been dissolved to any great extent; in one, the Mount Morgan mine, the solution of gold is clearly indicated. Even where the conditions for the solution of gold are most favorable, however, it is probably precipitated mainly in the upper part of the chalcocite zone. It would not remain in solutions that contain much ferrous sulphate, and chalcocitization is attended by abundant ferrous sulphate.

Silver, like copper, dissolves somewhat readily in a sulphuric acid environment, especially if ferric sulphate is present. Silver sulphide is not so soluble as copper sulphide, however (see p. 117), and in the presence of chlorides its downward migration is delayed by its precipitation as cerargyrite, or in the presence of ferrous sulphate or in contact with several sulphides and gangue minerals native silver is deposited. Some of the great copper lodes of Butte, Mont., were worked for silver to depths from 200 to 400 feet below the surface, where the deposits changed to rich copper ore.[2] Like gold, silver would be precipitated from sulphate solutions in an environment where chalcocite forms. Its sulphide is even less soluble than copper sulphide and in depth would be precipitated as argentite. Moreover, chalcocite readily precipitates gold and silver from chloride

[1] Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., vol. 1, no. 2, Chemistry series, p. 112, 1914.

[2] Emmons, S. F., The secondary enrichment of ore deposits, in Pošepný, Franz, The genesis of ore deposits, pp. 442–443, 1902.

and sulphate solutions. The rich narrow chalcocite zones at Ducktown, Tenn., contained considerable silver, although the primary pyrrhotite ore is only slightly argentiferous. In the north vein, Mass II, at Rio Tinto, Spain,[1] both gold and silver were concentrated in a thin layer just above the zone of copper and iron sulphides.

As already stated, both gold and silver are precipitated from dilute solutions by ferrous sulphate, but copper sulphate and ferrous sulphate may exist in the same solution without precipitation of copper. Although gold may be precipitated with chalcocite, it is not so likely that under similar conditions native copper and chalcocite are precipitated simultaneously. In the deeper zone, where sulphur or sulphides are in excess, both copper and silver are precipitated as sulphides rather than as native metals.

The rate at which certain sulphides react with acid to generate hydrogen sulphide and the tendency of certain ores to delay the downward migration of copper has already been discussed (p. 152). The precipitation of gold and silver, if any were held in the copper sulphate solution, would be more rapid than copper.

Carbonates react with solutions of sulphuric acid even more rapidly than pyrrhotite and likewise tend to delay the solution and downward migration of copper and gold. If there is much calcium carbonate in the gangue of the ore or in the wall rock, the downward migration of metallic sulphates may be checked or even inhibited. As stated by Bard,[2] chalcocitization is seldom extensive in carbonate rocks, because the copper is precipitated as carbonate by reaction with calcite. To this there are some exceptions, and, appreciating these, Bard notes that the precipitation of some copper carbonate on the limestone may inhibit further action and insulate the passages from reaction with the descending solutions. Under such conditions copper sulphate could descend through carbonate rocks to considerable depths, where it could be precipitated by iron sulphide or by hydrogen sulphide if any were generated by the action of acid on sulphides.

In some districts the primary mineralization of limestone is attended by extensive silicification. If carbonate has been removed, it would, of course, be no longer effective.

A gangue of siderite, dolomite, or other carbonates would also react with sulphuric acid solutions and tend to neutralize them, and thus to delay solution or to cause precipitation of gold or copper.[3]

[1] Vogt, J. H. L., Problems in the geology of ore deposits, in Pošepný, Franz, op. cit., p. 676.

[2] Bard, D. C., Absence of secondary copper sulphide enrichment in calcite gangue: Econ. Geology, vol. 5, pp. 59–61, 1910.

[3] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 743, 1914.

SOLUTION OF COPPER.

Pyrite, pyrrhotite, chalcopyrite, and bornite are commonly present in copper sulphide deposits, and nearly all copper deposits contain two or more of these minerals. They are generally the principal sulphides in the primary ore, and they are also present in the secondary ore, for residual masses of primary ore, not yet dissolved, will generally remain in the secondary sulphide zones. In the presence of oxygen and water these minerals are oxidized, setting free ferrous and ferric sulphates and sulphuric acid:

$$FeS_2+7O+H_2O=FeSO_4+H_2SO_4.$$
$$FeS+4O=FeSO_4.$$
$$CuFeS_2+8O=CuSO_4+FeSO_4.$$
$$Cu_5FeS_4+2H_2SO_4+18O=5CuSO_4+FeSO_4+2H_2O.$$

Some zinc blende that is rich in iron, (Zn,Fe)S, would also produce ferrous sulphate on weathering. Ferrous sulphate in the presence of oxygen changes to ferric sulphate.

$$6FeSO_4+3O+3H_2O=2Fe_2(SO_4)_3+2Fe(OH)_3.$$
$$2FeSO_4+H_2SO_4+O=Fe_2(SO_4)_3+H_2O.$$

Ferric sulphate is an active solvent of nearly all natural sulphides, and it dissolves nearly all the common metals except gold. It dissolves copper sulphides very readily, more readily, indeed, than sulphuric acid and free oxygen. The reactions may be written:

$$Fe_2(SO_4)_3+Cu_2S=CuSO_4+2FeSO_4+CuS.$$
$$Fe_2(SO_4)_3+CuS+3O+H_2O=CuSO_4+2FeSO_4+H_2SO_4.$$
$$Fe_2(SO_4)_3+CuS=CuSO_4+2FeSO_4+S.$$
$$2Fe_2(SO_4)_3+CuFeS_2=CuSO_4+5FeSO_4+2S.$$
$$Fe_2(SO_4)_3+FeS_2=3FeSO_4+2S.$$

In the oxidizing zone the sulphur is converted to sulphuric acid and sulphur dioxide, and consequently not much accumulates in that zone. Though these reactions are doubtless more simple than those that take place in nature, they represent the beginning and some of the end products of the processes and indicate the general tendencies of the superficial changes.[1]

[1] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, 50 pp., 1901. Buehler, H. A., and Gottschalk, V. H., The oxidation of pyrite: Econ. Geology, vol. 3, p. 532, 1908. Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides: Econ. Geology, vol. 5, p. 15, 1912. Lindgren, Waldemar, Copper deposits of Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 180, 1905. Allen, E. T., Sulphides of iron and their genesis: Min. and Sci. Press, vol. 103, p. 414, 1911. Tolman, C. F., Secondary sulphide enrichment of ores: Min. and Sci. Press, vol. 106, p. 140, 1913. Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 621, 1913.

In the oxidation of the copper sulphides, both primary and secondary, not all the copper is dissolved and removed, but semistable compounds or minerals are formed. These include, as stated above, the native metal, chlorides, sulphates, carbonates, silicates, and oxides of copper. That these minerals are only moderately stable in an oxidizing sulphate environment is indicated by their absence or rarity in the gossans of many sulphide deposits. They are almost entirely absent above some of the copper deposits at Butte, Mont.; Ducktown, Tenn.; Morenci, Ariz., and at many other copper deposits, and in nearly all districts containing copper sulphide ores they are more abundant near the secondary sulphide zone than at the surface. Except the sulphate and cupric chloride, all have very low solubilities in water. They are more soluble, however, in hydrochloric and in sulphuric acid and would be attacked by the small amounts of acid contained in mineral waters.

It has been shown (p. 305) that chlorine is the natural solvent of gold in processes of superficial alteration and that transfer of gold by chloride solutions is of economic importance in some deposists. But gold is some 2,000 times as valuable as copper, and transfers of small amounts of gold would be of commercial importance, whereas transfers of equal amounts of copper would be unimportant. Nevertheless transfers as chloride may take place. The zeolitic native copper deposits of the Lake Superior region are said to have been somewhat richer near the surface than at depths, and Lane[1] has suggested that enrichment has been effected by chloride waters. Moreover, sodium chloride is found in the lower levels of the Lake Superior mines in considerable concentrations. The solution of copper by sodium chloride is exceedingly slow, however, as is indicated by the use of that metal for covering seagoing vessels, and the copper transferred in chloride solutions of the concentration found in the mine waters of sulphide deposits must be exceedingly small.

Carbonate solutions likewise dissolve copper very sparingly, as is indicated by the comparatively stable carbonates of copper. The solubility is about 1 part in 3,333 parts water, saturated with carbon dioxide. The green crusts that form on copper that has been long exposed to the weather are mainly the basic carbonate, and the collection of these crusts in streaks indicates a certain mobility of the alteration product. Read[2] showed that copper is dissolved in small amounts by calcium bicarbonate. About 108 cubic centimeters of a solution containing 0.15 gram per liter of calcium bicarbonate was

[1] Lane, A. C., Salt water in the Lake mines: Lake Superior Min. Inst. Proc., vol. 12, p. 161, 1906.

[2] Read, T. T., The secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 37, p. 290, 1906.

placed in a 150 cubic centimeter flask, with 10 grams ground chalcopyrite (40–100 mesh) that had previously been tarnished with cupric sulphate, and was shaken daily for one month. The copper-iron sulphide showed a loss of 0.1 per cent and the solution contained a little copper. A sulphate was present in the filtrate, however, showing that the loss may have been due partly to oxidation. Free[1] has shown that water with carbon dioxide dissolves the basic copper carbonate in presence of calcium sulphate and sodium chloride; that large amounts of sodium chloride or sulphate increase solubility, and that sodium carbonate or calcium carbonate decreases solubility.

Tolman and Clark[2] showed that malachite, azurite, and chrysocolla, in the presence of an alkali, are slightly soluble in water containing carbon dioxide. Into a gas-washing bottle was put 1 gram of 200-mesh chrysocolla and 100 cubic centimeters water, into a second bottle 1 gram of 200-mesh azurite and 100 cubic centimeters water, and into a third 1 gram of 200-mesh azurite and 100 cubic centimeters one-half normal potassium carbonate. Carbon dioxide was passed through each bottle very slowly for 96 days. The liquid in the first bottle contained 0.0004 gram copper; the liquid in the second contained 0.0007 gram copper, and the liquid in the third 0.0007 gram. With excess carbon dioxide under heavy pressure carbonate solution is a more active solvent. The pressures in the upper part of the oxidized zone, however, are generally atmospheric pressures.

All the data given above indicate that water solutions containing alkali chlorides and carbonates are but feebly effective as solvents of the oxides, carbonates, and silicates of copper, and the other copper compounds that commonly accumulate in the lower parts of the oxidized zone. Except chalcanthite, which is soluble in water, these minerals are doubtless dissolved principally by sulphates. Sulphuric acid[3] reacts so readily on malachite, azurite, and chrysocolla that copper in them may be recovered commercially by acid leaching. Brochantite also, as is shown by experiments on ores from Chuquicamata, Chile,[4] is readily attacked by sulphuric acid, and yields an increase of acid on precipitation. Croasdale[5] states that sulphuric acid will extract but half the copper from cuprite.

[1] Free, E. E., The solubility of precipitated basic copper carbonate in solutions of carbon dioxide: Am. Chem. Soc. Jour., vol. 30, pp. 1366–1374, 1908.

[2] Tolman, C. F., jr., and Clark, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions and the dispersion and precipitation of copper sulphides from colloidal suspensions, with a geological discussion: Econ. Geology, vol. 9, p. 564, 1914.

[3] Croasdale, Stuart, The action of iron sulphides on copper solutions: Eng. and Min. Jour., vol. 97, p. 746, 1914.

[4] Leaching copper ores in Chile (anonymous): Min. and Sci. Press, vol. 106, p. 933, 1913.

[5] Croasdale, Stuart, Leaching experiments on the Ajo ores: Am. Inst. Min. Eng. Trans., vol. 49, p. 618, 1915.

The principal source of the sulphuric acid in the upper parts of the oxidized zones is doubtless pyrite. This mineral is the most stable of the iron sulphides under oxidizing conditions, and between fractures and cavities where it is not readily accessible to ground water a little is preserved, in some deposits to the very gossan. The most thoroughly weathered gossans with which I am familiar—those at Ducktown, Tenn.—contain a fraction of 1 per cent of sulphur. In western deposits one may frequently find a little pyrite at the outcrops by breaking the more solid and less altered country rock adjoining the oxidized lodes, and it is not at all uncommon in the harder and less altered parts of the weathered lodes themselves.

Other sources of sulphuric acid are the basic iron sulphates, such as jarosite. Although these are fairly stable in the oxidizing zones they ultimately break down or are partly dissolved, forming iron oxides and releasing their sulphate radicle. Thus it appears that sources of sulphuric acid are adequate to accomplish the leaching of the oxides and related copper minerals in the upper parts of the weathered zones. The simpler reactions, dissolving malachite, azurite, chrysocolla, and brochantite, respectively, may be thus stated:

$$CuCO_3.Cu(OH)_2+2H_2SO_4=2CuSO_4+3H_2O+CO_2.$$
$$2CuCO_3.Cu(OH)_2+3H_2SO_4=3CuSO_4+4H_2O+2CO_2.$$
$$CuO.H_4SiO_4+H_2SO_4=CuSO_4+H_4SiO_4+H_2O.$$
$$4CuO.SO_3.3H_2O+3H_2SO_4=4CuSO_4+6H_2O.$$

The oxides may be dissolved as follows:

$$Cu_2O+2H_2SO_4+O=2CuSO_4+2H_2O.$$
$$CuO+H_2SO_4=CuSO_4+H_2O.$$

Or with ferrous sulphate:

$$Cu_2O+2FeSO_4+H_2SO_4=Fe_2(SO_4)_3+H_2O+2Cu.$$

The native metal is dissolved with acid:

$$Cu+H_2SO_4+O=CuSO_4+H_2O.$$

The equations stated above are intended to show merely the general nature of the reactions. Any ferrous sulphate or sulphur dioxide present would unite with any oxygen present and be converted to ferric sulphate and sulphuric acid, thus further aiding solution. Ferric sulphate, which is found almost universally where copper ores are leached in the presence of atmospheric oxygen, probably aids in the solution of all copper minerals.

PRECIPITATION OF COPPER.

The superficial alteration of copper, as indicated above, may yield from a simple ore—for example, from one composed of chalcopyrite

and pyrite—many secondary minerals. In most deposits there is a fairly definite segregation of the minerals of the oxidizing zone—the native metal, sulphates, silicates, carbonates, and oxides; and the secondary copper sulphides and copper-iron sulphides. It is true that the oxidized zone commonly penetrates the secondary sulphide zone along fissures and water channels, but the oxidized minerals play out in depth, generally above the bottom of the secondary sulphide zone. The secondary sulphides that are found in the oxidized zone are generally to be regarded as the residuals of a former sulphide zone that is not yet completely oxidized.

We should therefore consider two sets of conditions—one where acid, free oxygen, and some ferric sulphate are present, and one where acidity is decreased, where there is no free oxygen, where ferrous salts predominate, and where primary sulphides occur in considerable quantities. On the following pages the occurrence and genesis of the minerals of the oxidizing zone are considered in some detail. The reactions there stated are summarized below for comparison.

Yielding native copper:

$$Cu_2S+4Fe_2(SO_4)_3+4H_2O=Cu+CuSO_4+8FeSO_4+4H_2SO_4.$$

Yielding brochantite:

$$2Cu_2S+10O+4H_2O=H_6Cu_4SO_{10}+H_2SO_4.$$

Yielding malachite and azurite:

$$2CuSO_4+2H_2Ca(CO_3)_2 = CuCO_3.Cu(OH)_2+2CaSO_4+3CO_2+H_2O.$$

$$3CuSO_4+3H_2Ca(CO_3)_2=2CuCO_3.Cu(OH)_2+3CaSO_4+4CO_2+2H_2O.$$

Yielding chrysocolla:

$$CuSO_4+H_2Ca(CO_3)_2+H_4SiO_4=CuOH_4SiO_4+CaSO_4+H_2O+2CO_2.$$

Yielding cuprite:

$$2Cu_2S+O=2CuS+Cu_2O.$$

It is noteworthy that these reactions use up oxygen, ferric sulphate, or bicarbonate. The equations merely represent the beginning and end products of the reactions, which are doubtless more complicated than the equations indicate. All these salts are dissolved in a strong excess of acid, and their solution is aided by ferric sulphate. They are consequently dissolved from the outcrops and the upper parts of the oxidized zones, where the acidity of solutions is less readily decreased because acid has already dissolved and carried away the ore and gangue minerals that are most readily

attacked and that therefore more readily reduce the acidity of the solutions. These minerals of the oxidizing zone therefore, as stated before, must be considered transition phases, not permanently stable. But in deposits that carry relatively little iron as sulphides, the common sources of acid, the oxidized ores are dissolved slowly and may accumulate at the very surface, as at Ajo, Ariz., where, according to Joralemon,[1] disseminated ores in porphyry are highly stained with copper at the surface but have a relatively small zone of chalcocite.

Further evidence of the instability of the copper minerals where exposed during long periods of weathering at the surface is their comparatively rare occurrence in sluice boxes of placers formed in a temperate climate. In the far north, however, the copper minerals show greater stability and the sulphides are found in stream gravels.[2]

At the greater depths copper is precipitated as copper sulphides or as copper-iron sulphides. The carbonates and silicates are not deposited at great depths, though it is a well-established fact that deep underground waters carry silica and carbonates. Even in limestone rocks the chalcocite zone is generally deeper than the zone of copper carbonate and associated minerals. This problem offers an attractive field for experimental study. Indeed some qualitative experiments of Spencer[3] and Nishihara[4] have a bearing on it. Spencer states that calcite does not precipitate copper from a solution containing both cupric and ferrous sulphate, but that in such a solution, in the presence of much calcite, pyrite and chalcopyrite may be coated with films of a secondary copper sulphide.[5] Nishihara repeated this experiment, making also one in which no calcite was introduced, and found that calcite not only did not inhibit the precipitation of copper sulphide but, if the solution is acid, by reduction of acidity the calcite accelerates precipitation of the sulphide. If ferric sulphate is added to the solution any bornite formed is quickly dissolved, but after the calcite has removed ferric sulphate (by precipitation of limonite and gypsum) the copper sulphide is again deposited, owing again doubtless to reduction of acidity and state of oxidation of the solution. The function of carbonates in halting the downward migration of copper is discussed on page 173.

[1] Joralemon, I. B., The Ajo copper-mining district: Am. Inst. Min. Eng. Trans., vol. 49, p. 601, 1915.

[2] Moffit, F. H., and Maddren, A. G., Mineral resources of the Kotsina-Chitina region, Alaska: U. S. Geol. Survey Bull. 374, 1909. Moffit, F. H., and Capps, S. R., Geology and mineral resources of the Nizina district, Alaska: U. S. Geol. Survey Bull. 448, p. 89, 1911. Winchell, H. V., Prospecting in the North: Min. Mag., vol. 3, p. 204, 1910.

[3] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 648, 1913.

[4] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 750, 1914. Also, Importance of carbonates in the rôle of secondary enrichment: Econ. Geology, vol. 9, p. 483, 1914.

[5] Spencer, A. C., op. cit., p. 649.

There are many data relating to the precipitation of secondary sulphides of copper, chalcocite, covellite, bornite, and chalcopyrite, as well as to their synthesis and their occurrence in ore bodies. Although some of the data are conflicting, the general nature of the processes is indicated.

Winchell[1] placed crystals of pyrite in a sealed jar in a slightly acid solution, containing sulphur dioxide and a dilute solution of copper sulphate. At the end of three months films of chalcocite were deposited on the pyrite, and its copper content, which at the beginning was 1.50, had increased to 3.60 per cent. In another jar, with similar reagents except sulphur dioxide, no chalcocite was deposited. Winchell suggests that sulphur dioxide is necessary for the deposition of cuprous sulphide. He infers that the cupric sulphate in solution with sulphur dioxide supplies cuprous ions for the reaction with the pyrite that supplies the sulphur for the chalcocite, the iron going into solutions as ferrous salt. He found that iron was dissolved and subsequently precipitated as ferric hydrate.

The inference that cuprous ions form in this reaction has not received universal acceptance, because cuprous salts have not been identified in mine waters. Cuprous sulphate is a very unstable compound. It may be held in solution in some substances, but when placed in water it quickly becomes cupric sulphate. Recently, however, Wells[2] has shown that cuprous ions may exist in exceedingly small concentration under conditions nearly similar to those that prevail where sulphate waters attack iron and copper sulphides. Examination of eight mine waters collected by the writer failed, however, to reveal a trace of cuprous salt.

Oxygen tends to delay or to inhibit the precipitation of copper sulphides. Possibly the difference in the behavior of the two chemical systems above described, one with and the other without sulphur dioxide, is due in part also to the power of sulphur dioxide to remove atmospheric air from the solution. The oxygen would be removed to form sulphuric acid, and copper sulphide would then be more readily precipitated by pyrite. In the jar without sulphur dioxide enough oxygen may have been present to effectively delay precipitation.

Another point which should be considered in this connection is the acidity of the solutions from which precipitation was attempted. Mr. F. F. Grout[3] has repeated Winchell's experiment, with excess of acid and with careful exclusion of atmospheric oxygen, but after three years there is little change in the sulphides introduced.

[1] Winchell, H. V., Synthesis of chalcocite and its genesis at Butte, Mont.: Bull. Geol. Soc. America, vol. 14, pp. 272–275, 1903.

[2] Wells, R. C., The fractional precipitation of sulphides: Econ. Geology, vol. 5, p. 12, 1910.

[3] Grout, F. F., unpublished data.

Sullivan[1] also repeated the experiments of Winchell. Forty cubic centimeters of cupric sulphate solution containing 0.1 gram of copper and saturated with sulphur dioxide lost its color almost at once on shaking with 20 grams of finely powdered chalcopyrite, but cupric sulphate without sulphur dioxide, similarly treated, became colorless only at the expiration of a week. To each of the colorless solutions 4 cubic centimeters of a cupric sulphate solution was then added, containing 0.250 gram of copper. On standing overnight the solution containing sulphurous acid was again colorless, and the color of the solution containing no sulphur dioxide faded very slowly. In similar experiments with pyrite and cupric sulphate, one in the presence of and one in the absence of sulphurous acid, the copper at the end of three days had been practically all precipitated from the solution that contained cupric sulphate and sulphurous acid (H_2SO_3), while from the solution that contained cupric sulphate alone about 0.040 gram of copper had been precipitated out of a total of 0.097 gram of copper in 40 cubic centimeters.

These experiments show that the quantity of copper precipitated on pyrite varies with concentration of acid and that high acidity is not favorable to precipitation of secondary copper sulphide on pyrite or chalcopyrite. T. T. Read[2] also repeated Winchell's experiments and found that there was a small loss of copper and gain of iron in solution when 10 grams powdered chalcopyrite was treated with 108 cubic centimeters of cupric sulphate containing 3 grams copper per liter, but this was much increased by addition of sulphur dioxide.

Stokes[3] states that cupric sulphate reacting with pyrite yields sulphuric acid, as is indicated in the following equation, one which has been widely accepted as representing the process of chalcocitization of pyrite:

$$5FeS_2+14CuSO_4+12H_2O=7Cu_2S+5FeSO_4+12H_2SO_4.$$

Welsh and Stewart, by treating chalcopyrite with dilute cupric sulphate for three months, obtained a tarnish, probably of copper sulphide.[4]

A. C. Spencer found that bornite reacts with cupric sulphate and gives a film which is probably covellite. This subsequently changes to the color of chalcocite.[5] Chalcopyrite with cupric sulphate alone is not readily affected, but with both ferrous sulphate and cupric

[1] Sullivan, E. C., Discussion of paper by T. T. Read on The secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 37, p. 893, 1906.

[2] Read, T. T., Secondary enrichment of copper-iron sulphides: Am. Inst. Min. Eng. Trans., vol. 33, p. 299, 1906.

[3] Stokes, H. N., Experiments on the actions of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, p. 23, 1907.

[4] Welsh, T. W. B., and Stewart, C. A., Note on the effect of calcite gangue on the secondary enrichment of copper veins: Econ. Geology, vol. 7, p. 785, 1912.

[5] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 625, 1913.

sulphate a film was observed which changed in color from bronze to pink, purple, indigo, and steel blue. The final coating was cupric sulphide. The reaction did not take place in the presence of a little sulphuric acid in four months. As shown by H. V. Winchell,[1] acidified copper sulphate and copper sulphate without sulphur dioxide had not deposited copper sulphate on pyrite at the end of two years.

Spencer expresses the belief that chalcocitization generally involves several stages, from chalcopyrite through bornite and covellite to chalcocite. Krusch, as well as Graton and Murdoch, have noted a closely similar paragenesis, and Ransome, at Superior, Ariz., noted the series in ascending order: Pyrite, chalcopyrite, chalcocite. The series pyrite, chalcopyrite, bornite, chalcocite, was noted by Gilbert and Pogue in ores at Mount Lyell, Tasmania. In that region there is less probability that the deposit was formed by descending waters, since the tetrahedrite, enargite, and chalcopyrite were formed after chalcocite, and their genesis is said to be uncertain. In the Leonard mine at Butte, according to Ray,[2] the paragenesis is pyrite, enargite, covellite, chalcocite, bornite, and some chalcopyrite, followed by a later generation of chalcocite. This series, except the later generation of chalcocite, he believes, however, to represent deposition by ascending thermal waters. (See p. 168.)

Spencer, discussing the pyrite-chalcocite series, tabulated below, writes many equations showing how members of this series, by reacting with cupric sulphate, may become richer in copper and poorer in iron, finally reaching the chalcocite stage. It is noteworthy that acid and ferrous sulphate are almost always shown as formed in these equations. Stokes, who accomplished these syntheses[3] in the presence of sulphuric acid (p. 166), proved quantitatively the increase of acid.

Pyrite-chalcocite series.

Pyrite	FeS_2.
Chalcopyrrhotite	$CuFe_4S_6$.
Barracanite	$CuFe_2S_4$.
Cubanite	$CuFe_2S_3$.
Chalcopyrite	$CuFeS_2$.
Barnhardtite	$Cu_4Fe_2S_5$.
Bornite (1)	Cu_5FeS_3.
Bornite (2)	Cu_5FeS_4.
Bornite (3)	Cu_9FeS_6.
Covellite	CuS.
Chalcocite	Cu_2S.

[1] Winchell, H. V., op. cit., p. 272.

[2] Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, p. 463, 1914.

[3] Stokes, H. N., op. cit. See U. S. Geol. Survey Prof. Paper 43, p. 183, where this equation is discussed by Lindgren; also Beck, R., The nature of ore deposits, translated by W. H. Weed, vol. 2, p. 380, where the chemistry of copper enrichment is treated by E. C. Sullivan; and Spencer, A. C., Chalcocite enrichment: Washington Acad. Sci. Jour., vol. 3, p. 73, 1913; Econ. Geology, vol. 8, pp. 621–652, 1913.

Paragenesis of some copper sulphide ores.

1 Morenci.[a]	2 Superior.[b]	3 Ely, Nev.[c]	4 Mount Lyell.[d]	5 Butte.[e]	6 "Common."[f]	7 "As a rule."[g]
Chalcocite.	Chalcocite.	Chalcocite.	Chalcocite.	Chalcocite.	Chalcocite.	Chalcocite.
				Bornite.		
				Chalcopyrite.		
				Chalcocite.		
Covellite.		Covellite.		Covellite.	Covellite.	
	Bornite.	Bornite.	Bornite.	Bornite.	Bornite.	Bornite.
	Chalcopyrite.	Chalcopyrite.	Chalcopyrite.		Chalcopyrite.	Chalcopyrite.
				Enargite.		
Sphalerite.	Pyrite.		Cupriferous pyrite.	Pyrite.	Pyrite.	Pyrite.

[a] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 183, 1905.
[b] Ransome, F. L., Copper deposits near Superior, Ariz.: U. S. Geol. Survey Bull. 540, p. 149, 1912.
[c] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 627, 1913.
[d] Gilbert, C. G., and Pogue, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., p. 618, 1913.
[e] Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, p. 463, 1914. R. H. Sales states that bornite is a transition product between pyrite and chalcocite but some bornite he states is primary and formed after chalcocite (Econ. Geology, vol. 5, p. 682, 1910).
[f] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper: Am. Inst. Min. Eng. Trans., vol. 45, p. 39, 1914.
[g] Krusch, P., Primäre und sekundäre Erze unter besonderer Berücksichtigung der "gel" und der "schwermetallreichen" Erze: Cong. géol. internat., 12th session, Toronto, Canada, p. 281, 1914.

Copper sulphide is precipitated also by pyrrhotite, sphalerite, and galena. All these minerals may be replaced by chalcocite or by covellite. The reactions set forth involve no changes of valence.

$$FeS+CuSO_4=CuS+FeSO_4.$$
$$ZnS+CuSO_4=CuS+ZnSO_4.$$
$$PbS+CuSO_4=CuS+PbSO_4.$$

The first two equations represent common processes. Where galena precipitates copper, lead sulphate is probably formed, and its low solubility would tend to delay the reaction. Examples of replacement of iron, iron-copper, zinc, and lead sulphides are mentioned on page 138.

Dilute cold sulphuric acid reacting on sulphide minerals evolves hydrogen sulphide. The action is most rapid with alabandite and pyrrhotite, but, as shown by Wells,[1] it goes on with sphalerite and galena, and at a slightly higher temperature (41° C.), according to Clark,[2] it is accomplished very slowly with pyrite, chalcopyrite, and bornite. Hydrogen sulphide will readily precipitate copper from sulphuric acid solutions, on account of the low solubility of copper sulphide. It will likewise precipitate copper sulphide from neutral or alkaline solutions.

Grout[3] has shown that dilute solutions of either alkali carbonates, alkali hydroxides, or alkali silicates, one or all of which probably accumulate at great depths, will react with the various metallic sul-

[1] Wells, R. C., in U. S. Geol. Survey Bull. 529, p. 59, 1912.
[2] Clark, J. D., A study of the enrichment of copper sulphide ores: New Mexico Univ. Bull., Chemistry ser., vol. 1, No. 2, p. 116, 1914.
[3] Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold, with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 429, 1913.

phides and form alkali sulphide (Na_2S or K_2S). These sulphides, like hydrogen sulphide, react with copper sulphate, causing precipitation of copper sulphide. Moreover, these sulphides with antimony or arsenic will form double sulphides of alkalies and arsenic or antimony, which will precipitate silver antimony sulphide and probably such cupriferous double salts as tetrahedrite and possibly enargite.

Stokes's equations showing the precipitation of copper sulphide in acid solutions have been widely credited, and it is generally supposed that chalcocite is formed in an acid environment. That chalcocite may be deposited in an alkaline environment is indicated above, however, by chemical experiments cited; these are supported by field observation. In chalcocite ore from Mount Morgan, Queensland, which I have recently examined, through the courtesy of Mr. H. Eidemiller, the copper sulphide which replaces pyrite contains numerous crystals of calcium carbonate. (See p. 345.) In a solution more than very slightly acid this carbonate would have been dissolved, and it is highly improbable that reactions generating acid, such as are indicated in many equations showing the precipitation of chalcocite, would simultaneously precipitate calcium carbonate. The deposition of chalcocite takes place in neutral and alkaline as well as in acid solutions, and on pyrite and chalcopyrite more readily in alkaline solutions.

RÉSUMÉ OF BASIC OBSERVATIONS.

Mineral waters in sulphide ores near the surface are solutions of sulphuric acid and ferric sulphate. With increase of depth the acidity of such solutions decreases and ferrous sulphate accumulates. At greater depths the waters become neutral and ultimately they become alkaline. Copper in practically all its compounds is dissolved by sulphuric acid in the presence of air, and particularly in the presence of ferric sulphate. Cupric sulphate is formed. Copper sulphide may be precipitated from cupric sulphate solutions in the presence of sulphuric acid and ferrous sulphate but not in the presence of much ferric sulphate. Copper is dissolved in the presence of only a little ferric sulphate, but the solubility product for the system, comprising cupric, ferrous, and ferric sulphates, in the presence of a soluble sulphide, has not been worked out. Precipitation takes place simultaneously with solution of nearly all other sulphides, and the common sulphides—those of lead, zinc, and iron, all of which are below copper in the Schuermann series—are replaced by copper in its deposits. Hydrogen sulphide formed by the action of acid on many sulphides, and alkaline sulphides formed by the action of dilute alkalies on many sulphides, will precipitate copper from its solutions. Although copper is precipitated in the presence of sulphuric acid, on pyrite it is more readily precipitated in a nearly neutral, or neutral, or in an alkaline environment.

OUTCROPS OF COPPER DEPOSITS.

As already stated, the upper part of the oxidized zone of a copper sulphide deposit may be so thoroughly leached that practically all the copper is removed and carried downward. As the upper part of the oxidized zone becomes by erosion the outcrop, it follows that the outcrops of copper sulphide deposits, if erosion is slow and the conditions for leaching are favorable, may be practically barren of copper. In base-leveled countries or in countries where the surface has remained nearly stationary for a long time, the outcrops are generally depleted of copper. Even in mountainous countries, where erosion is comparatively rapid, not many large deposits of copper are workable at the surface. Ferric sulphate hydrolyzes, depositing limonite, so the deposits of many iron-copper sulphide ores are marked by a gossan or "iron hat." Many copper deposits have been discovered by following downward a nearly barren gossan or by the downward exploitation of deposits of precious metals that are concentrated near the surface above deposits of copper ores in which the precious metals are present in but small amounts. Examples of deposits showing such changes are given on page 157.

In copper deposits that do not carry sulphides the downward transportation of copper is generally slow. The native copper deposits of Keweenaw Point, Mich., are workable at the surface, although the country has undergone erosion for a period so long that it has become nearly a peneplain.

Where the sulphides are present in subordinate quantities copper carbonates and silicates may occur abundantly at and near the surface, as at Ajo, Ariz.,[1] where oxidized copper minerals are conspicuous in outcrops.

In limestone copper will commonly segregate as carbonate at and near the surface, and many oxidized copper deposits in limestone have been worked by open pits. Limestones that have been altered by contact metamorphism are relatively impermeable, because their tough, heavy silicates, such as garnet, amphibole, and mica, are not readily fractured. Most such deposits contain considerable calcite, and any copper-iron sulphides they carry will usually oxidize to carbonates, silicates, and oxides. The copper in such an ore is particularly stable and is likely to endure long weathering. Such deposits have stimulated deep prospecting in many districts where other types of deeper copper ores are present,[2] and they have thus served as useful indicators of hidden wealth. Garnet zones have been worked as open pits in the Morenci-Metcalf district, Arizona; in the Bullion

[1] Joralemon, I. B., The Ajo copper-mining district: Am. Inst. Min. Eng. Trans., vol. 49, p. 601, 1915.

[2] Emmons, W. H., The outcrops of ore deposits, in Bain, H. F., and others, Types of ore deposits, p. 318, San Francisco, 1911.

district, Nevada; at Patagonia, Ariz.; and at many other places. In some places secondary sulphides, partly oxidized, occur at the surface.

The copper lodes in igneous rocks at Butte are leached of copper, some of them to a depth of 400 feet. The disseminated ores in porphyry show great variation as to depth of leaching, but are commonly leached to depths of 100 to 300 feet below the surface, and exceptionally at greater depths. Some of them show practically no copper at the surface. At Cananea, Sonora, and Morenci, Ariz., barren gossans that were explored to considerable depths have led to good deposits of chalcocite ore. Copper was only sparingly present at most places in the outcrops of the great disseminated deposits at Miami and Ray, Ariz. At Bingham it was locally somewhat conspicuous as carbonates and silicates.

It is noteworthy that some gossans that have been followed far downward have led to no copper sulphide ore below. A pyritic primary deposit not containing sufficient copper will oxidize without concentration of copper ores in the sulphide zone.

In making explorations for copper the question frequently is raised whether drilling is justified in an area that shows but little iron oxide at the surface. Nearly all copper deposits in North America do show ferruginous outcrops, but some gossans that cap valuable disseminated ores in porphyry are not heavily stained with iron. At Cananea, Sonora, valuable chalcocite deposits occur below outcrops that show heavy iron stain only here and there. As a rule, however, the outcrops show much silicification and kaolinization and more or less limonite. Of the outcrops at Morenci Lindgren says:[1]

> Such "iron caps" as are seen at the outcrops of veins in regions where oxidation proceeds undisturbed by erosion are generally absent in this district. The veins are rather marked by siliceous outcrops containing a small amount of oxidized copper ore and little limonite; some of them are entirely barren. The ore bodies in limestone contain, it is true, much limonite, but that is rather due to reactions between sulphate and carbonate than to direct oxidation.

TRANSPORTATION OF COPPER AND DEPTHS TO WHICH SECONDARY ENRICHMENT OF COPPER MAY BE EFFECTIVE.

It has already been shown that the copper migrates downward by stages, and may be carried into solution and precipitated again and again, its behavior depending on the chemical environment, that is, on the state of oxidation and the acidity of the solutions, which, again, depend on nearness to the surface. In an oxidizing acid environment copper that has been precipitated will be redissolved; in a reducing, less acid environment it will be precipitated.

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, pp. 179–180, 1905.

The deposition of secondary copper sulphides will depend on the depths to which oxidation has extended. There may not everywhere be a secondary sulphide zone below the zone of oxidation, but there is evidently a general relation between oxidation and secondary sulphide enrichment. The depth of oxidation depends on many factors, among them permeability of the ore, climate, topography, duration of period of weathering, rate of erosion, and character of ore and of the gangue. In the heavy pyrrhotite ores at Ducktown, Tenn., the maximum depth of oxidation in nearly all the lodes is about 100 feet. At Encampment, Wyo., it is 100 feet or more. At Morenci oxidation in sphaleritic copper sulphide ore is generally 50 to 200 feet deep. At Butte, Mont., oxidation is 300 to 400 feet deep; at Bingham, Utah, it is only 300 feet deep in the Highland Boy mine but 1,450 feet deep in the Brooklyn mine. At Globe, Ariz., oxidation is general at depths of 700 or 800 feet and locally extends to much greater depths. In the White Oaks region, N. Mex., it is about 1,380 feet deep. In deposits in limestone at Tintic, Utah, it is 2,400 feet deep.

In deposits containing copper-iron sulphides secondary copper sulphides will generally form at depths below the zone of active oxidation, although to some extent the oxides may be associated with sulphides. Secondary chalcocite is deposited at slight depths below the surface in ores carrying much pyrrhotite. At Ducktown it is generally found within 100 feet of the surface. In the pyrrhotitic deposits at Encampment, Wyo., secondary copper sulphides lie 200 feet or more below the surface. At Morenci secondary chalcocite ores are found 400 feet or more below the surface; at Ely the average depth of the bottom of ores developed in porphyry is about 325 feet; but in the Alpha mine enriched ore is as deep as the 1,200-foot level. At Globe secondary copper ore is found as deep as the 1,600-foot level of the Old Dominion mine. On the Live Oak ground at Miami it was found at depths below 1,000 feet. At Ray the chalcocite ore extends to depths of 700 feet. At Butte chalcocite ores are found below the 3,000-foot levels, but probably such ore is not secondary. Weed[1] states, however, that the deposition of chalcocite by descending water on the 2,200-foot level of the Mountain Con mine was interrupted only by the opening of the mine workings.

INFLUENCE OF ORE AND GANGUE MINERALS ON DEPTHS OF SECONDARY SULPHIDE ZONES.

As already stated, the depth of the secondary sulphide zone depends on climate, topography, duration of period of weathering, permeability, composition of ore, and other factors. These factors

[1] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 164, 1912.

must be weighted for each deposit or group of deposits, but certain relations of mineral composition to depth are often the controlling ones and these will be emphasized here.

Bard[1] first called attention to the fact that as calcite precipitates copper as carbonate, the downward migration of copper in limestone would be thus delayed. Later Spencer[2] showed that in the presence of calcite, ferrous sulphate, and cupric sulphate, chalcopyrite will develop films of copper sulphide. As it has been shown, however, that ferric sulphate inhibits the precipitation of copper sulphide and that decrease of acidity and development of alkaline conditions favor precipitation of copper sulphide on pyrite, and as both the state of oxidation and the acidity of descending waters are reduced in presence of calcite, it follows that a gangue of calcite will delay the downward migration of copper. Other carbonates, particularly siderite, as shown by Nishihara,[3] readily decrease the acidity and reduce the state of oxidation of acid ferric sulphate solutions.

Silicification of limestone removes carbonate and by weathering also calcite is rapidly eliminated. Indeed the most deeply oxidized zones are in limestones. Moreover, though the elimination of carbonates is aided by sulphuric acid generated by iron sulphide, it occurs also in the absence of iron pyrite. The most deeply oxidized iron deposits known to me are those of the Newport mine on the Gogebic iron range, Mich., which owe their workability to the oxidation of a cherty iron carbonate. There sideritic protore[4] has been completely decarbonated at depths of 2,700 feet measured on the incline, and more than 2,400 feet vertically below the surface. At Tintic, Utah, copper deposits in limestone have been oxidized 2,400 feet below the surface. Nevertheless, if we inspect the various deposits of North America with these premises in view, we find that the deepest extensive secondary chalcocite zones are not in limestone nor in ores that carry much carbonate in the gangue. The deepest extensive chalcocite zones in limestone are those of Bisbee, where, in the Lowell mine, secondary chalcocite is found at a depth of 1,600 feet. But Ransome[5] has shown that in this district secondary deposits were formed before the beds were tilted to their present positions, indeed before the Cretaceous rocks were deposited. They are there-

[1] Bard, D. C., Absence of secondary copper sulphide enrichment in calcite gangue: Econ. Geology, vol. 5, pp. 59–61, 1910.

[2] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 648, 1913.

[3] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 753, 1914.

[4] Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 242, 1911.

[5] Ransome, F. L., Notes on the Bisbee district, Arizona: U. S. Geol. Survey Bull. 529, p. 179, 1913.

fore related not to the present topography and the present water level but to an ancient surface that was long ago covered by later rocks.

Ores carrying much pyrrhotite are not enriched at great depths below the oxidized zone. This conclusion is justified by field experience and by much experimental data. Among the common sulphides the position of pyrrhotite is unique; it will decrease acidity,[1]

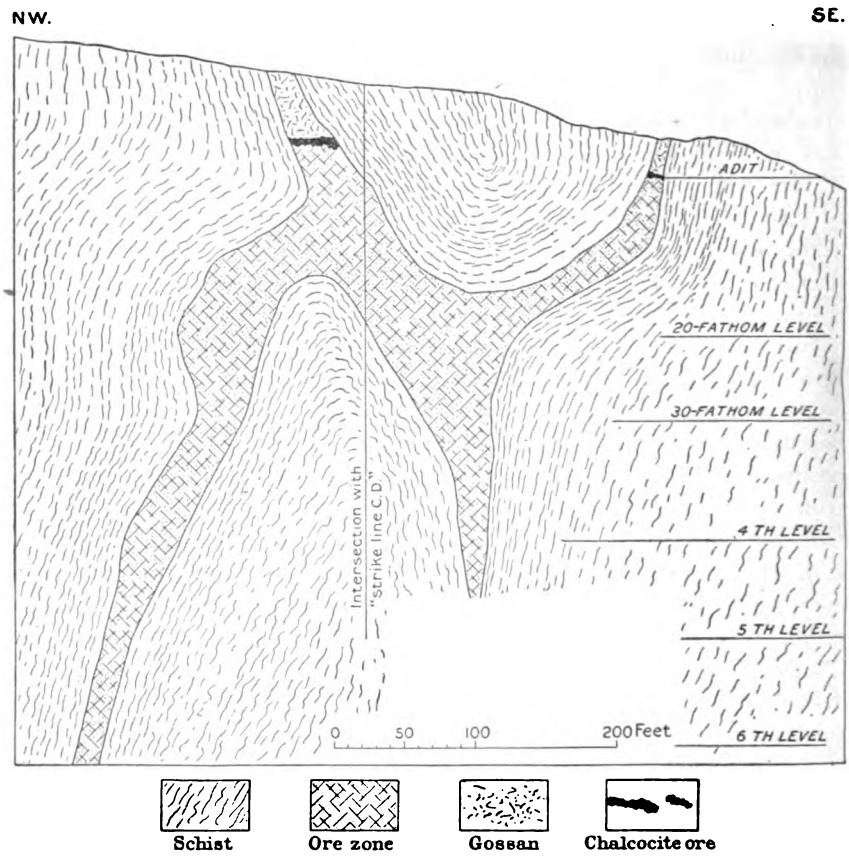


FIGURE 13.—Cross section of the Mary lode, Ducktown, Tenn. After W. H. Emmons and F. B. Laney. In this deposit of pyrrhotite ore the chalcocite zone is exceptionally thin.

reduce ferric sulphate,[2] and generate hydrogen sulphide[3] more rapidly than any other common sulphide. Even in alkaline solutions it will react with the alkalies to form alkaline sulphides more rapidly than other common minerals. In every series of reactions that tends toward precipitation of copper as sulphide its activity is rapid. Alabandite would likewise delay the downward transfer of copper, but it is not an abundant mineral, and if present only in small

[1] Nishihara, G. S., op. cit., p. 753.
[2] Grout, F. F., op. cit., p. 427.
[3] Wells, R. C., U. S. Geol. Survey Bull. 529, p. 59, 1913.

amounts it would generally be used up quickly and would then be no longer effective. Sphalerite reacts with acid solutions to liberate hydrogen sulphide more readily than pyrite or chalcopyrite, and it is replaced by copper sulphide before pyrite, but it reacts less readily than pyrrhotite. Pyrite and chalcopyrite react more slowly than any of the common sulphides.

As stated on page 153, the vertical extent of the secondary sulphide zone in pyrrhotite deposits is relatively small. (See fig. 13.) In sphaleritic deposits without pyrrhotite it is more extensive vertically

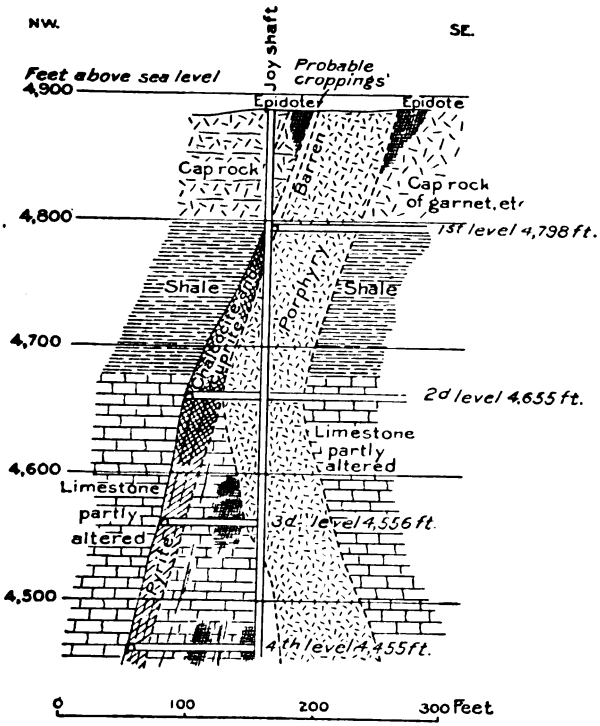


FIGURE 14.—Cross section of Joy vein, Morenci district, Arizona. After Waldemar Lindgren. The primary ore carries pyrite, chalcopyrite, and sphalerite but no pyrrhotite.

(see fig. 14), and in thoroughly fractured deposits of pyrite and chalcopyrite with little or no sphalerite or pyrrhotite the secondary sulphide zone may be much more extensive vertically. (See Pl. VI.)

Secondary zones of only moderate vertical extent should be expected in deposits that carry much arsenopyrite and tetrahedrite. I know of no secondary copper sulphide zone in leucite or nepheline rocks, but if such a zone is found without much doubt it will not extend far below the zone of oxidation because the feldspathoids decrease acidity so readily. All basic rocks are unfavorable to deep enrichment except when thoroughly altered.

OCCURRENCE OF THE COPPER MINERALS.

Native copper occurs in the Lake Superior district and in zeolitic lodes elsewhere as the principal primary copper mineral. In the sulphide ores of the Cordillera of North America native copper is confined to the upper zone of the ore bodies and is clearly secondary. It is formed in many places by the reduction of cuprite and is frequently found, with copper oxides, directly above the zone of secondary chalcocite ores. A. F. Rogers[1] described a specimen of native copper from the Calumet & Arizona mine, Bisbee, Ariz. Cubes modified by octahedral and dodecahedral faces occur in cavities of a limonite gangue. The native metal there he believes replaces cuprite.

The following reactions forming native copper from cuprite appear probable:

$$Cu_2O+H_2SO_4=H_2O+Cu_2SO_4.$$
$$Cu_2SO_4+2FeSO_4=2Cu+Fe_2(SO_4)_3.$$

Or expressed as one equation:

$$Cu_2O+2FeSO_4+H_2SO_4=2Cu+Fe_2(SO_4)_3+H_2O.$$

At Cananea, Mexico, at Cashin, Colo., and at many other places tabular masses of native copper cut the decomposed oxidized ore, suggesting the possibility that it has altered directly from chalcocite. At Morenci, Ariz., it is associated with cuprite, as a rule in the upper limit of the chalcocite zone. In the Williams vein, Arizona Central mine,[2] in this district, 200 feet below the surface, a vein of solid copper was found in sericitized porphyry. The vein formed a sheet of copper, in places 8 inches thick, standing nearly vertical. It had in places a fibrous structure, perpendicular to the plane of the vein, such as occasionally is exhibited by the chalcocite seams, of which it is believed to be a pseudomorphic development. In one specimen, according to Lindgren, two sheets of copper were found separated by sooty chalcocite. According to Graton and Murdoch[3] native copper forms directly from chalcocite in some ore of the Old Dominion mine, Globe, Ariz.

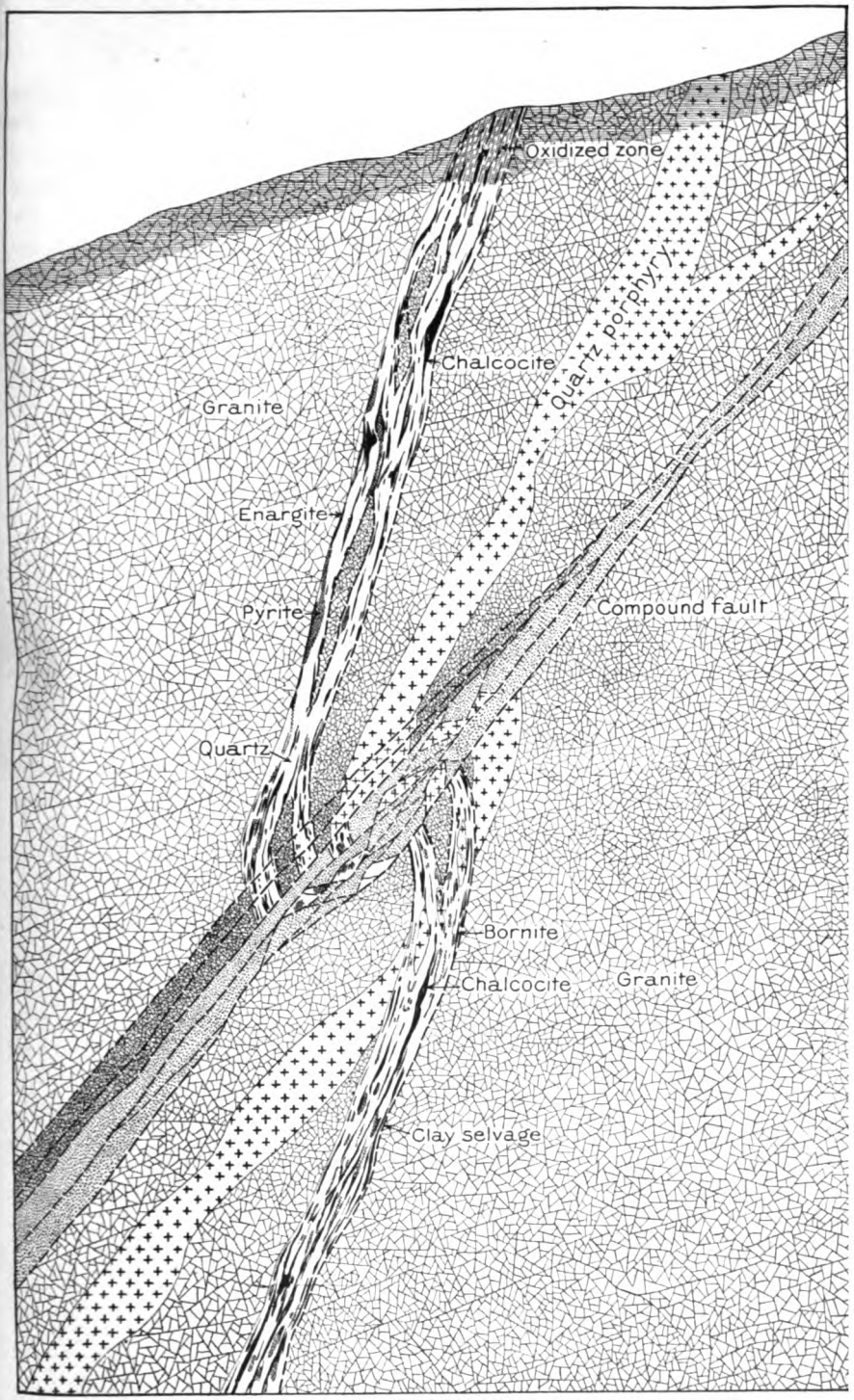
In view of these relations it appears that copper may form directly from chalcocite without the intermediary stage of oxidation to cuprite. Lindgren suggests this reaction:

$$Cu_2S+3Fe_2(SO_4)_3+4H_2O=2Cu+6FeSO_4+4H_2SO_4.$$

[1] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 17, 1910.

[2] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 101, 1905.

[3] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 56, 1914.



IDEAL CROSS SECTION OF ANACONDA VEIN, BUTTE, MONT.

After H. V. Winchell.

An equation in which not all of the copper is reduced to native metal in the presence of ferric sulphate may be written:

$$Cu_2S+4Fe_2(SO_4)_3+4H_2O=Cu+CuSO_4+8FeSO_4+4H_2SO_4.$$

Native copper was abundant above the third level of the Copper Queen ore body at Bisbee, Ariz., but comparatively rare in the lower portions of the oxidized ores.[1] In the Calumet & Arizona mine, however, it is abundant on the 1,050-foot level. It occurs in part as incrustations of chalcocite. As Ransome (see p. 209) has shown, these deposits have been tilted since they were oxidized. At Bingham, Utah,[2] native copper is rare but has been observed. Some native copper is present in most of the mines at Tintic, Utah, but generally in small amounts. A specimen from the Boss Tweed mine showed native metal surrounded by cuprite.[3] Much native copper is developed in the upper zones of copper deposits at Santa Rita, N. Mex. In general, it is abundant from 100 to 200 feet below the surface. According to Lindgren, Graton, and Gordon[4] it is probably an alteration product of sulphides, but the latter appear to have been deposited in part in open spaces in the porphyry rather than as replacements of pyrite. In this district and also in the copper deposits of Lake Superior native copper has been found as pseudomorphs after hornblende. According to Yeates,[5] native copper in Grant County, N. Mex., is pseudomorphous after azurite. Native copper is not abundant at Butte, Mont.,[6] nor at Park City, Utah.[7] At Ducktown, Tenn., according to report, where mines that had been closed during the Civil War were reopened masses of native copper were found hanging to some of the timbers.[8]

In view of the fact that ferrous sulphate, a reducing agent, probably accumulates at depths at which chalcocite forms, one would suppose that native copper, which is a product of reduction, might be deposited under some conditions along with chalcocite; this association is common but is probably due to subsequent oxidation of

[1] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 120, 1904.

[2] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 110, 1905.

[3] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 701, 1898.

[4] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 316, 1910.

[5] Yeates, W. S., Pseudomorphs of native copper after azurite, from Grant County, N. Mex.: Am. Jour. Sci., 3d ser., vol. 38, pp. 405–407, 1889.

[6] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 80, 1912.

[7] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 106, 1913.

[8] Edwards, W. F., Discussion of a paper by H. A. Lee on Gases in metalliferous mines: Colorado Sci. Soc. Proc., vol. 7, p. 183, 1904.

chalcocite and reduction to native copper. In the deeper parts of the zones of alteration sulphur, in the primary minerals, generally occurs in abundance and consequently the secondary copper minerals that form there are sulphides.

Chalcanthite (blue vitriol), $CuSO_4.5H_2O$, is commonly present in the oxidized zones as efflorescences of stalactites on open fissures, or as veinlets filling small crevices above the upper limit of the zone of secondary sulphides. At Ducktown, Tenn., it is abundant also in the chalcocite zone and constitutes a valuable ore mineral. It rarely forms far below the top of the chalcocite zone, except on surfaces of openings made by mining operations. At Butte, Mont., according to Weed,[1] it coats rock fragments in old stopes, in places so abundantly that it has been found profitable to collect it from time to time. In the Silverbow mine pure chalcanthite is so abundant as to almost fill some of the old drifts. Beautiful stalactites and shapes imitating organ pipes are developed. At Horn Silver mine, Utah, chalcanthite is abundant on the eleventh, the lowest level examined.[2] At some other mines, also, it is found at considerable depths. It occurs sparingly on the 1,600-foot and 1,700-foot levels in the Ontario mine, Park City, Utah.[3] In Butte copper deposits, according to Weed, copper sulphate is carried by the moisture of the atmosphere circulating in mine openings.[4]

Pisanite, $(Cu,Fe)SO_4.7H_2O$, is a rare sulphate of copper and iron. Large and beautiful specimens were found in copper deposits at Bingham, Utah.[5] At Butte, Mont., stalactites occur, usually in deserted drifts.[6] It occurs sparingly, according to Van Horn,[7] at Ducktown, Tenn.

Brochantite, $H_6Cu_4SO_{10}$, a basic sulphate of copper, has been identified at only a few places. It is of common occurrence in the ores of the Clifton-Morenci district, Arizona, where, according to Lindgren,[8] it is intergrown with malachite, which effectively masks its presence in hand specimens. In the Shannon mine, near the surface, in porphyry, it constitutes a rich ore body. Brochantite has been found at Tintic, Utah.[9] Ransome noted it also in thin sections

[1] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 81, 1912.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 108, 1913.

[3] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 115, 1913.

[4] Weed, W. H., op. cit., p. 99.

[5] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 111, 1905.

[6] Weed, W. H., op. cit., p. 82.

[7] Oral communication.

[8] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 119, 1905.

[9] Hillebrand, W. F., and Washington, H. S., Notes on certain rare copper minerals from Utah: U. S. Geol. Survey Bull. 55, p. 47, 1885.

from the oxidized zone at Bisbee, Ariz., and it is found in oxidized ores of the Horn Silver mine, Utah,[1] and the Cerro Gordo mine, California.[2] At Chuquicamata, Chile,[3] it is the principal mineral in one of the largest copper deposits in the world. This deposit, which has been proved to depths of 1,000 feet in places, changes with depth to chalcocite, bornite, and chalcopyrite. About three-fourths of the ore developed is brochantite and one-fourth is sulphides. In all its occurrences brochantite is probably deposited by oxidizing waters.

Sullivan[4] obtained a substance of the composition of brochantite by treating silicates with copper sulphate solutions. Lindgren[5] states that brochantite may form directly by the oxidation of chalcocite according to the following reaction:

$$2Cu_2S+10O+4H_2O=H_6Cu_4SO_{10}+H_2SO_4.$$

Atacamite and nantokite.—Atacamite, $CuCl_2.3Cu(OH)_2$, the oxychloride of copper, and nantokite, CuCl, cuprous chloride, are comparatively rare secondary copper minerals. They are probably formed in the oxidized zones, but on account of their solubility in natural waters they do not generally accumulate. In the arid region near the western coast of South America, atacamite has been reported from several places. At Chuquicamata, Chile,[3] it has been supposed to be abundant, but recently this ore has been proved to be mainly brochantite. In the United States the natural chlorides of copper are almost unknown.

Malachite, $(CuOH)_2CO_3$, a basic cupric carbonate, is abundant in the oxidized zones of many cupriferous deposits and is most abundant in deposits that are inclosed in limestone. It was present in considerable quantity in the superficial portions of copper deposits at Bingham, Utah,[6] where it occurs as globular masses and also as bands equivalent to parts of certain rock strata. It also forms envelopes about sulphides and oxides. In the Old Dominion mine at Globe, Ariz., according to Ransome,[7] malachite is conspicuously developed as veinlets in quartzite and has locally replaced the quartzite. At Park City, as stated by Boutwell,[8] malachite is found

[1] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 106, 1913.

[2] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 105, 1914.

[3] Editorial, Min. and Sci. Press, vol. 106, p. 933, 1913.

[4] Sullivan, E. C., The interaction between minerals and water solutions: U. S. Geol. Survey Bull. 312, p. 61, 1907.

[5] Lindgren, Waldemar, op. cit., p. 188.

[6] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 107, 1905.

[7] Ransome, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, p. 122, 1903.

[8] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 112, 1913.

in cracks in quartzite at stopes on the 1,200-foot level of the Silver King mine. In this district malachite occurs also as a coating on gray copper.

Malachite is present almost universally also in the oxidized zones of cupriferous sulphide deposits in rocks other than limestones and in some of them it persists in the outcrops. In the Philipsburg district, Montana,[1] in lodes inclosed in granite, malachite generally occurs in the oxidized zones of silver deposits that carry a little chalcopyrite and tetrahedrite. At Butte it is only sparingly developed in most of the oxidized ore. In the San Francisco district, Utah, malachite was an important mineral in the O K and Lady Bryan mines.[2] The former is in quartz monzonite; the latter in limestone.

The association of malachite with limonite in the gossan has encouraged deep development in many copper districts. It is unknown as a primary ore in deposits formed by thermal waters.

If copper sulphate waters should mingle with acid carbonate waters, the following reaction[3] would probably take place:

$$2CuSO_4+2H_2Ca(CO_3)_2=CuCO_3.Cu(OH)_2+2CaSO_4+3CO_2+H_2O.$$

Acid waters attacking limestone would form malachite according to the following reaction:

$$2CuSO_4+2CaCO_3+5H_2O = CuCO_3.Cu(OH)_2+2CaSO_4.2H_2O+CO_2.$$

Solutions of iron sulphate and copper sulphate react with limestone and deposit limonite and malachite simultaneously.[4]

Malachite may readily be obtained synthetically also by bringing carbonate solutions into contact with metallic copper. The mineral has been identified on many coins that have been buried for long periods.[5] On Chinese copper coins of a dynasty of the seventh century, Rogers[6] found malachite coated with azurite. In sulphuric acid solutions copper carbonates are dissolved freely, and more freely in the presence of ferric sulphate. Wells showed that copper is precipitated in alkaline carbonate solutions more readily than the other common metals except mercury and lead.[7] That copper carbonate is almost insoluble in alkaline carbonate solutions is shown

[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 157, 1913.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 100, 1913.

[3] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 24, 1906.

[4] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, pp. 189–190, 1905.

[5] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 663, 1916.

[6] Rogers, A. F., Minerals observed on buried Chinese coins of the seventh century: Am. Geologist, vol. 31, p. 45, 1903.

[7] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

also by experiments of J. D. Clark, who exposed it for many days in presence of alkaline carbonates and CO_2 with only trivial loss.[1]

Azurite, $2CuCO_3.Cu(OH)_2$, like malachite, is a basic cupric carbonate. So far as known, it is not formed by ascending thermal waters. It is very much less abundant than malachite, but in some deposits in limestone, as at Bisbee, Ariz., it is plentiful. Kemp[2] suggests the following reaction with copper sulphate and acid carbonate solutions:

$$3CuSO_4 + 3H_2Ca(CO_3)_2 = 2CuCO_3.Cu(OH)_2 + 3CaSO_4 + 4CO_2 + 2H_2O.$$

Azurite may form in the gossan and oxidized zone, even in ore deposits that contain only a little copper.[3] At Park City, Utah,[4] azurite is somewhat less rare than the green carbonate. In the Silver King mine, in a stope between the 800-foot and 900-foot levels, there was a solid bed of azurite one-fourth to one-half inch thick, and below the stope copper carbonate stains or replaces lead carbonate. Tetrahedrite also is coated with azurite. At Morenci it is frequently associated with kaolin[5] and is generally one of the last minerals to form.

In limestone azurite may be formed according to the following reaction:

$$3CuSO_4 + 3CaCO_3 + 7H_2O = 2CuCO_3.Cu(OH)_2 + 3CaSO_4.2H_2O + CO_2.$$

Rogers[6] described occurrences of azurite on ancient Chinese copper coins recently exhumed. On three of the coins the succession was copper, cuprite, malachite, and azurite. Azurite was, however, less abundant than malachite.

Chrysocolla, $CuOH_4SiO_4$, the bluish-green hydrous copper silicate, forms rather abundantly in the outcrops and near the surface of some copper deposits, though in others it is rare or absent. Of 62 analyses, according to Foote and Bradley,[7] only 12 agree with the formula stated above. These investigators regard chrysocolla a "solid solution" of $CuSiO_3$ and H_2O, its composition depending on conditions of formation. Chrysocolla is a common mineral in the

[1] Clark, J. D., A chemical study of the enrichment of copper sulphide ores: New Mexico Univ. Bull. 75, p. 103, 1914.

[2] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 24, 1906.

[3] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 157, 1913.

[4] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 112, 1913.

[5] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 118, 1905.

[6] Rogers, A. F., Minerals observed on buried Chinese coins of the seventh century: Am. Geologist, vol. 31, p. 45, 1903.

[7] Foote, H. W., and Bradley, W. M., On solid solution in minerals: Am. Jour. Sci., 4th ser., vol. 36, p. 180, 1913.

oxidized zone of some silver and gold mines. Although widely distributed in some lodes, it occurs at most places only in small bodies. It is commonly associated with malachite and azurite and is not known as a deposit of ascending hot waters. At Globe, Ariz.,[1] chrysocolla replaces dacitic tuff. In this district it is older than malachite where the two minerals are together and it forms at greater depths than malachite. It is an ore mineral in several other deposits of the Southwest, where it is mined with copper oxides and carbonates. At Bisbee it is only sparingly present. At Butte, Mont.,[2] it is found in the country rock near the veins. Chrysocolla is abundant in veins and decomposed country rock at Tintic, Utah.[3] It is common in the secondary ores of the San Francisco region, Utah,[4] and occasionally present at Park City.[5] It is known also in the Cerro Gordo mine, Inyo County, Cal.[6] At Philipsburg, Mont., it is not abundant but occurs here and there in the upper levels of several mines.[7] Minute specks are common in oxidized copper ores. At Cripple Creek chrysocolla is an oxidation product of tetrahedrite.[8]

There is no record of the synthesis of chrysocolla in the laboratory. Kemp[9] has suggested that it results from gelatinizing silica and solutions of copper sulphate:

$$CuSO_4 + H_2Ca(CO_3)_2 + H_4SiO_4 = CuOH_4SiO_4 + CaSO_4 + H_2O + 2CO_2.$$

In the Coppereid district, Nevada, according to Ransome,[10] it has replaced limestone.

According to Rogers, calcite scalenohedrons at Arlington, N. J.,[11] and calcite rhombohedrons at the Reward gold mine, Inyo County, Cal., are replaced by chrysocolla. The rhombohedrons are made up of concentric layers of varying shades of blue. It appears, however, that abundant carbonate is not uniformly a condition for its genesis,

[1] Ransome, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, p. 123, 1903.

[2] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[3] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 701, 1898.

[4] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 105, 1913.

[5] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 112, 1913.

[6] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 106, 1914.

[7] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 162, 1913.

[8] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 129, 1906.

[9] Kemp, J. E., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, pp. 24–25, 1906.

[10] Ransome, F. L., Notes on some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 65, 1909.

[11] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 20, 1910.

since in the Morenci district, Arizona,[1] it is more abundant in the ores in porphyry and in granite than in the ores in limestone. In some deposits in porphyry it is of commercial value. An interesting occurrence of highly auriferous chrysocolla is that of the Original Bullfrog mine in Nevada. If in the reaction suggested by Kemp ferrous acid carbonate were present in place of that of lime, ferrous sulphate would form instead of calcium sulphate. Minute quantities of ferrous sulphate drive gold from solutions in which it is dissolved as chloride. Possibly the free gold of chrysocolla was precipitated by ferrous sulphate.

In the Calumet & Arizona mine chrysocolla forms thin shells about kernels of cuprite, native copper, and brochantite and is in turn enveloped by malachite and calcite.[2]

Chrysocolla incrusts cuprite in the Yellow Pine district, Nevada,[3] and it replaces cuprite also in the ores from the Santa Margarita mine,[4] New Almaden, Cal., and from the Tintic district, Utah. A specimen from the Calumet & Arizona mine, Bisbee, Ariz., described by Koenig,[5] consists of melanchalcite forming thin envelopes about kernels of cuprite and inclosed in turn by chrysocolla.

Chrysocolla is itself moderately soluble in dilute sulphuric acid.[6] The reaction is rapid enough to be used on a commercial scale. In alkaline solutions[7] and excess carbon dioxide at ordinary pressures chrysocolla is very slowly soluble.

Dioptase, H_2CuSiO_4 or $H_2O.CuO.SiO_2$, like chrysocolla, is a secondary copper silicate. It is characteristically formed in the zone of oxidation and is unknown as a deposit from hot ascending waters. It is known in only a few places in the United States, among them Morenci Ariz.,[8] where it is associated with chrysocolla in limestone.

Turquoise, probably $Cu_2O.Al_2O_3.2P_2O_5.9H_2O(?)$, is not a common oxidation product of copper ores but appears to form under conditions where copper salts are formed along with those of phosphorus. As apatite is fairly abundant in some of the disseminated copper deposits, it is surprising that turquoise is not more common. The

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 112, 1905.

[2] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 126, 1904.

[3] Hill, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, p. 246, 1914.

[4] Rogers, A. F., op. cit., p. 20.

[5] Koenig, G. A., On the new species of melanchalcite and keweenawite: Am. Jour. Sci., 4th ser., vol. 14, pp. 404–409, 1902.

[6] Austin, W. L., The leaching of copper ores at the Steptoe works, Nevada: Am. Inst. Min. Eng. Trans., vol. 49, p. 669, 1915.

[7] Tolman, C. F., jr., and Clark, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions and the dispersion and precipitation of copper sulphides from colloidal suspensions, with a geological discussion: Econ. Geology, vol. 9, p. 564, 1914.

[8] Lindgren, Waldemar, op. cit., p. 111.

best known deposits in the United States yielding turquoise are near Tyrone, about 10 miles southwest of Silver City, N. Mex. There turquoise is inclosed in intruded granite and quartz monzonite where these rocks have been deeply eroded and extensively weathered.[1] The turquoise is in veins filling cracks in the altered granite and nuggets or concretions of turquoise are embedded in kaolin.[2] Associated minerals are malachite and chrysocolla, and veins of quartz and jarosite cut the turquoise. Below the zone of oxidation turquoise is absent and not much material of value is found below depths of 100 feet. The minerals found at depths are pyrite, quartz, sericitized feldspar, and apatite.[3] Zalinsky thinks the turquoise deposits were formed by the agency of heated waters, but Paige regards them as products of normal weathering.

Cuprite, Cu_2O, is a common mineral of the oxidized zones of deposits of copper sulphides and is probably secondary in all its occurrences. The capillary or hairlike form is known as chalcotrichite.

Cuprite is an important ore mineral at Bisbee, Ariz., where, according to Ransome,[4] it is found in an impure earthy condition mixed with limonite and ferruginous clays or in crystalline masses associated with native copper. The latter occurrence is particularly characteristic of the deeper oxidized zones in the vicinity of chalcocite and other sulphides. In the Calumet & Arizona mine cuprite is found in large crystalline masses. On the 950-foot level it occurs in bunches in earthy ore, penetrated by dendritic masses of metallic copper and spotted with little vugs of acicular malachite. It is abundant at Morenci, Ariz., at Cananea, Sonora, and in other western districts. At Morenci, according to Lindgren,[5] it occurs normally at the upper limit of the chalcocite zone as a product of decomposition of chalcocite. Similar relations are shown at Cananea. At Santa Rita, N. Mex., abundant cuprite and native copper fill fissures in the oxidized zone and presumably are secondary in the main after chalcocite. At Butte, Mont., where it is sparingly developed and is not important commercially,[6] it generally contains masses of native copper, the line of contact between them being indistinct.[7] According to Boutwell,[8] cuprite is not abundant at Bingham, Utah, but

[1] Paige, Sidney, The origin of turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 7, p. 382, 1912.

[2] Zalinski, E. R., Turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 2, pp. 464–492, 1907.

[3] Paige, Sidney, op. cit., p. 387.

[4] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 128, 1904.

[5] Lindgren, Waldemar, op. cit., p. 106.

[6] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 80, 1912.

[7] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[8] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 109, 1905.

small grains covered with malachite were noted in brown altered limestone of the Commercial mine. It is rare also at Park City, Utah.[1] Cuprite is present in the upper part of the rich secondary ore at Ducktown, Tenn., and in other copper deposits of the southern Appalachians. At Morenci, Ariz., the normal occurrence of cuprite is at the upper limit of the chalcocite zone as a product of decomposition of the latter.

The mode of its derivation from chalcocite is stated by Lindgren as follows:[2]

$$2Cu_2S+O=2CuS+Cu_2O.$$

Lindgren considers it improbable that ferrous sulphate reduces cupric sulphate to precipitate cuprous oxide, as cupric sulphate and ferrous sulphate appear to mix in all proportions without reaction.

Tenorite, CuO, the crystalline form of the black oxide of copper, is much less abundant than cuprite. The earthy, sooty variety, known as melaconite, is said to be present at Butte, Mont., where it is associated with cuprite and native copper and forms dark rims about cuprite.[3] According to Boutwell,[4] scales of black copper oxide with metallic luster occur with chalcocite in ores of Bingham, Utah. At Bisbee[5] melaconite is found in soft clayey ores on the 1,000-foot level of the Lowell mine. Apparently it is now being deposited along with wad near the 850-foot level of the Calumet & Arizona mine. At Tintic, Utah, melaconite is moderately abundant.[6] In this district it is said to form from various copper minerals and to be changed by reduction to form cuprite.

At Ducktown, Tenn., much of the so-called black copper ore has proved to be sooty chalcocite.

Copper pitch ore is a secondary material of complex character and somewhat uncertain composition. A sample from the Detroit mine in the Morenci district, Arizona,[7] analyzed by Hillebrand, showed oxides of copper, zinc, and manganese, with considerable water and silica. Material that is probably of a similar nature is found at Bisbee and at Courtland, Ariz., and on the Ida, Montgomery, and

[1] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 109, 1913.

[2] Lindgren, Waldemar, op. cit., p. 186.

[3] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[4] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 109, 1905.

[5] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 128, 1904.

[6] Tower, G. W., and Smith, G. O., Geology and mining industry in the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 701, 1898.

[7] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 114, 1905.

Amazon claims[1] at Butte, Mont. It occurs also in many of the copper ores of the San Francisco region, Utah.[2]

Chalcocite (copper glance), Cu_2S, is the most valuable copper mineral. In 1906, according to Graton,[3] 47 per cent of the copper produced in the United States was derived from chalcocite ores. In most of its occurrences chalcocite is clearly of secondary origin. It replaces other minerals metasomatically or occurs as veinlets in small cracks in the primary ore. Well-authenticated examples are known of its replacement of pyrite, chalcopyrite, covellite, bornite, enargite, zinc blende, and galena. In many deposits now worked in which chalcocite is the principal mineral exploration extends into the lower-grade primary sulphide ore, which generally consists of chalcopyrite, pyrite, and other minerals without chalcocite.

Examples indicating replacement of pyrite by chalcocite are numerous. At Morenci, Ariz., according to Lindgren, most of the ore bodies owe their origin to this process. He says:[4]

> By chalcocitization the massive veins of pyrite become transformed into solid masses of black dull chalcocite, while the sericitized porphyry becomes filled with grains and little seams of the same mineral. The first constitutes high-grade ores, the second the low grade. A residue of pyrite, not yet acted upon, is nearly always present. Thus a vein of massive sooty material cutting the shale in the Montezuma mine contained 96 per cent Cu_2S and 2.4 per cent FeS_2, and pyrite may be easily seen in nearly every specimen of low-grade porphyry ore. The pyrite first becomes coated with a black stain; in a more advanced stage the chalcocite penetrates the pyrite on cracks and fissures in all directions; finally it almost entirely replaces it. * * * Kaolin gouge always accompanies chalcocite when occurring as massive veins; in the chalcocitized porphyry the process is nearly always attended by a formation of a little brownish kaolin, together with microcrystalline quartz or more often chalcedony; these minerals encircle the pyrite or traverse the chalcocite as minute veinlets, distinctly later than the alteration of the porphyry to sericite and pyrite. Sericite does not form during chalcocitization; on the contrary, the kaolin is formed at the expense of that mineral. * * * The transition from chalcocite to unaltered pyrite at the lower limit of the zone is remarkably sudden. Usually a change takes place within 25 feet, sometimes within 10 feet, from rich chalcocite ore to pyrite with one-half to 1 per cent copper. Chalcopyrite is rarely found as a secondary mineral but has been observed as small grains inclosed in chalcocite veinlets.

At Bingham, Utah, according to Boutwell,[5] chalcocite incloses pyrite and chalcopyrite. At the Snowstorm and Park mines, in the Coeur d'Alene district, Idaho, chalcocite and bornite ore are disseminated in quartzite. At the Park mine chalcocite has formed on

[1] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 81, 1912.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 97, 1913.

[3] Graton, L. C., Copper: U. S. Geol. Survey Mineral Resources, 1906, p. 410, 1907.

[4] Lindgren, Waldemar, op. cit., p. 185.

[5] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, pp. 221–222, 1905.

pyrite and chalcopyrite.[1] In the Bisbee district, according to Ransome, chalcocite occurs as veinlets in and envelopes around grains of pyrite. Limestone altered to white claylike material is streaked with veinlets of chalcocite and speckled with native copper. Some solid, compact chalcocite is associated with bornite.[2] Chalcocite replaces pyrite in the O K mine, San Francisco region, Utah.[3]

Examples of replacement of pyrite by chalcocite could be cited from nearly every important district in the United States that produces copper sulphide ores. At Ely, Nev.,[4] according to Spencer, chalcocite extensively replaces chalcopyrite. Where pyrite and chalcopyrite occur together the chalcopyrite is generally most altered.

In the great copper deposits of Butte, Mont., chalcocite is an important ore mineral. The bulk of the ore is altered "granite" with disseminated grains and veinlets of chalcocite intergrown with pyrite or replacing that mineral completely. Distinct crystals are rare. In this district the history of the vein formation is exceedingly involved, and at least two periods of mineralization are recognized. The great chalcocite bonanzas in the upper levels at Butte were regarded by S. F. Emmons, W. H. Weed, H. V. Winchell, and others as secondary, and no other interpretation appears to be warranted by their occurrence and relations. More recently, however, masses of ore containing chalcocite have been found as deep as 2,800 feet below the surface, and Reno Sales[5] is of the opinion that a portion of the massive deep-seated chalcocite at Butte is of primary origin. The studies of polished surfaces examined microscopically by Simpson[6] of ore from the 2,000-foot level showed massive pyrite surrounding, in the plane of the section, small and apparently isolated flakes of chalcocite. A veinlet of ore from the 1,000-foot level of the Leonard mine shows isolated idiomorphic crystals of quartz and pyrite surrounded by chalcocite.[7]

Metallographic studies by Ray showed that chalcocite replaces covellite, enargite, and bornite and cements fragments of the earlier sulphides.[8] In the Mountain Con mine at Butte, according to

[1] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 91, 1908.

[2] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, pp. 123–124, 1904.

[3] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 93, 1913.

[4] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 642, 1913.

[5] Sales, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 681, 1910.

[6] Simpson, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, p. 634, 1908.

[7] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 76, 1912. For Weed's final conclusions see this bulletin, p. 205.

[8] Ray, J. C., Paragenesis of the ore minerals of the Butte district: Econ. Geology, vol. 9, p. 427, 1914.

Weed, sooty chalcocite and bornite were forming in minute fractures in ore and altered granite on the 2,200-foot level, third drift north, when that part of the mine was opened.[1]

L. C. Graton noted that chalcocite is found as deep as 970 feet in the Bully Hill mine, Shasta County Cal., where it seems to be below the zone of secondary sulphide enrichment. He says that "there is no reason to believe that it is secondary."[2]

According to Lewis,[3] chalcocite is the original ore of the Rocky Hill mine, in New Jersey, where it is found near intrusions of trap intimately associated with magnetite, hematite, and tourmaline. Near Pine City, Minn., veins of primary chalcocite are found in basalt flows. The chalcocite in the region of Christiania, Norway, is regarded by V. M. Goldschmidt[4] as in part a primary mineral.

The copper lodes of the Virgilina district, in Virginia and North Carolina, described by Laney,[5] are of peculiar interest in this connection. The country is an area of schists and gneisses intruded by granite and diabase. The deposits are fissure veins. The level of ground water is 50 to 75 feet below the surface and the zone of secondary alteration does not appear to extend below 250 feet. The important mines of the district are 350 to 500 feet deep and the ore from the deepest levels contains almost as much chalcocite as bornite.[6] The ores in the deeper levels show little secondary fracturing, and from this Graton[7] concluded that the chalcocite is in part of primary origin. Laney subsequently worked out the paragenesis of these ores by a microscopic study of polished surfaces. Some of his sections[8] show a crystallographic intergrowth of bornite and chalcocite in relations that suggest the intergrowth of quartz and feldspar in a graphic granite. Their intergrowth suggests that in this ore these two minerals are contemporaneous, and as the specimens were obtained from considerable depth in tight lodes it can not reasonably be supposed that the minerals were deposited by cold sulphate waters. Laney[9] concludes that—

> Chalcocite is clearly of two periods—one confined to the upper portions of the vein more recent than and filling a network of minute fractures in the

[1] Weed, W. H., Geology and ore deposits of Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 164, 1912.

[2] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, pp. 104–105, 1910. See also Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 76, 1914.

[3] Lewis, J. V., Copper deposits of the New Jersey Triassic: Econ. Geology, vol. 2, p. 247, 1907.

[4] Goldschmidt, V. M., Die Kontaktmetamorphose im Kristianiagebiet, p. 250, 1911.

[5] Laney, F. B., The relation of bornite and chalcocite in the copper ores of the Virgilina district of North Carolina and Virginia: Econ. Geology, vol. 6, pp. 399–411, 1911.

[6] Idem, p. 399.

[7] Graton, L. C., Copper: U. S. Geol. Survey Mineral Resources, 1907, pt. 1, p. 620, 1908.

[8] Especially that figured in his pl. 7, fig. 2, p. 406.

[9] Laney, F. B., op. cit., p. 411.

bornite; the other contemporaneous and intergrown, often crystallographically, with it. There is no evidence that any of the bornite is of secondary origin. It is therefore believed that in the Virgilina district the greater part of the chalcocite is a primary mineral contemporaneous with the bornite and in no way derived from it or from any other copper-bearing minerals by processes of secondary alteration.

Other examples of "graphic structure" shown by chalcocite and bornite are seen in ores from Mount Lyell, Tasmania, and Plumas County, Cal., mentioned on page 79. Not all investigators agree in their interpretations of the "graphic" intergrowths. It appears probable, however, that under some conditions chalcocite is deposited as a primary mineral by ascending hot waters. Ascending alkaline hot solutions are generally supposed to have deposited the primary ores of nearly all the larger copper deposits. Such solutions are doubtless variable in composition. It appears probable that under conditions where the concentration of iron is low in the solutions chalcocite may form as a primary mineral instead of chalcopyrite, which is the commoner primary ore.

The chalcocite deposits in sandstone and shale which are very widely distributed in the Southwest should be mentioned here. Many of these deposits are in areas remote from igneous rocks and appear not to be related genetically to igneous processes. They have doubtless been deposited by cold waters and some of them have replaced coal or other organic material. In New Mexico,[1] in Colorado,[2] and elsewhere, such deposits have formed where there is no evidence that a sulphide existed previously. In the "Red Beds" of Oklahoma, 10 miles northeast of Stillwater, in Payne County, according to W. A. Tarr,[3] veinlets of chalcocite are found cutting carbonaceous material. Barite is present in several of these ore bodies, suggesting the agency of sulphate solutions. Although these deposits are not secondary in the sense that they have formed at the expense of older sulphides, the conditions under which they were formed as regards temperature, pressure, and concentration of solution are probably near those which prevail in processes of sulphide enrichment. Indeed, in certain deposits in Oklahoma that have recently been described by Fath[4] chalcocite is shown to have replaced marcasite.

[1] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 76–77, 1910.

[2] Emmons, S. F., Copper in the red beds of the Colorado Plateau region: U. S. Geol. Survey Bull. 260, pp. 221–232, 1905. Emmons, W. H., The Cashin mine, Montrose County, Colo.: U. S. Geol. Survey Bull. 285, pp. 125–128, 1906. Lindgren, Waldemar, Notes on copper deposits in Chaffee, Fremont, and Jefferson counties, Colo.: U. S. Geol. Survey Bull. 340, pp. 157–174, 1908.

[3] Tarr, W. A., Copper in the "Red Beds" of Oklahoma: Econ. Geology, vol. 5, p. 223, 1910.

[4] Fath, A. E., Copper deposits in the "Red Beds" of southwest Oklahoma: Econ. Geology, vol. 10, p. 140, 1915.

The conditions which are assumed to exist where secondary chalcocite is precipitated have already been stated. The solutions contain copper sulphate and iron sulphate. Under some conditions the solutions are probably acid. Without much doubt the iron is in the ferrous state. Stokes's equations[1] indicate that ferrous salt is liberated in the reaction. Winchell[2] states that hematite does not form where solutions are acid, as at Butte. According to Ransome[3] the formation of chalcocite at Bisbee was effected without the development of ferric oxide as a by-product. At Globe Ransome did not detect hematite or ferric hydrate in microscopic intergrowths of pyrite-chalcocite ores. Lindgren emphasizes the presence of ferrous sulphate as an attendant of processes of chalcocitization at Morenci,[4] and this is suggested by analyses of waters from copper deposits of Ely, Nev.[5] One of the deeper waters collected by Lawson carried 9.36 grains per gallon of ferrous sulphate and only 0.4 grain per gallon of ferric sulphate.

Experiments in the precipitation of chalcocite have already been discussed. It is precipitated in acid solutions with hydrogen sulphide and in alkaline solutions with alkaline sulphide, and from a solution of cupric sulphate it is precipitated on iron sulphide. None of these experiments was carried out under exactly the conditions which probably exist in the secondary sulphide zone. Stokes's experiments (p. 166) were made at a high temperature and ferrous sulphate was not introduced. In Winchell's experiments the chalcocite was formed in the presence of sulphur dioxide, which, so far as is indicated by analyses available, appears to occur very sparingly, if at all, in waters from copper mines.

In the synthesis of chalcocite with pyrite, Stokes found that covellite was formed but subsequently changed to cuprous sulphide. (See p. 166.) Others have made similar observations. There are reasons for supposing that this takes place under conditions of sulphide enrichment, the cupric sulphide changing to cuprous sulphide in the presence of cupric sulphate and ferrous sulphate. The cuprous ion has been looked for in vain in at least 10 of the analyses of mine waters. On the other hand, Wells has shown that the cuprous ion probably does exist in exceedingly small concentration in solu-

[1] Stokes, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, p. 22, 1907. See also Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 183, 1905. Wells, R. C., The fractional precipitation of sulphides: Econ. Geology, vol. 5, p. 1, 1910.

[2] Winchell, H. V., The synthesis of chalcocite and its genesis at Butte, Mont.: Eng. and Min. Jour., vol. 75, pp. 783–784, 1903.

[3] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 157, 1904.

[4] Lindgren, Waldemar, op. cit., p. 186.

[5] Lawson, A. C., The copper deposits of the Robinson mining district, Nevada: California Univ. Dept. Geology Bull., vol. 4, p. 333, 1906.

tions of cupric and ferrous sulphate and the direct precipitation of chalcocite is by no means unlikely.

Spencer and others, as already noted, regard the transformation of iron sulphides to cuprous sulphide to be by steps, the series of "oxidations" being pyrite, chalcopyrite, bornite, covellite, chalcocite. In several districts, however, pyrite appears to change directly to chalcocite. More data on this synthesis are needed, especially some on the synthesis in an alkaline environment.

According to Posnjak, Allen, and Merwin,[1] cuprous sulphide is dimorphous, and its inversion temperature is about 91°. Orthorhombic chalcocite, when heated above 91°, becomes isometric, but when more than 8 per cent cupric sulphide is present the inversion does not take place and any isometric crystals formed above 91° would not become orthorhombic on cooling. All observed crystals, however, are orthorhombic and are therefore formed presumably below 91°.

Covellite, CuS, is found in small amounts in many mining districts of North America but is not abundant in many of the larger deposits. As a rule it is associated with chalcocite, and it is formed chiefly as a replacement of iron or zinc sulphides. Weed[2] estimates that covellite formed 0.5 per cent of the copper in the ore mined at Butte. In this region it is secondary and fills vugs in the quartz-pyrite veins and occurs as veinlets cutting the enargite ore. These relations have been noted by Weed in the Leonard mine as deep as the 1,100-foot level. J. C. Ray[3] has studied polished surfaces of a series of ores from the 1,600-foot level of this mine and finds covellite replacing enargite, sphalerite, and pyrite. This he considers, however, a deposit formed from ascending solutions. Graton and Murdoch[4] describe blades of covellite that penetrate pyrite at Butte and consider such occurrences primary. At Bor, Serbia, as at Butte, covellite replaces enargite and pyrite. There, according to Lazarevic, it is exclusively secondary and decreases with increase of depth, pyrite and enargite coming in lower.[5] Covellite replaces sphalerite at Morenci, Ariz.;[6] at the Poole mine,[7] in the Foothill copper belt of California; and at the Big Coon mine,

[1] Posnjak, E., Allen, E. T., and Merwin, H. E., The sulphides of copper: Econ. Geology, vol. 10, p. 526, 1915.

[2] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, pp. 72, 76, 1912.

[3] Ray, J. C., The paragenesis of the ore minerals at Butte, Mont.: Econ. Geology, vol. 9, p. 473, 1914.

[4] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 51, 1914.

[5] Lazarevic, M., Die Enargit-Covellin Lagerstätte von Cuka-Dulkan bei Bor in Ost-Serbien: Zeitschr. prakt. Geologie, vol. 20, p. 337, 1912.

[6] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 183, 1905.

[7] Rogers, A. F., A new synthesis and new occurrences of covellite: School of Mines Quart., p. 300, 1911.

Galena, Kans.[1] At Lake City, Colo.,[2] according to Irving and Bancroft, small masses of blue sulphide, on being broken into minute cleavage blocks, were found to be sphalerite thinly coated along the numerous cleavage surfaces with films of covellite. Covellite forms from sphalerite also at the Kyshtim mine, Russia.[3] Covellite is rather abundant in the San Francisco region, Utah.[4] Much is present in the Horn Silver mine, where it is a replacement of pyrite, zinc sulphides, and galena and an alteration of chalcocite. It replaces chalcopyrite in the O K mine and the Old Hickory mine.

Covellite is said to be primary in Shasta County, Cal.[5] Covellite fills cracks in galena and replaces it in ores of the Caledonia mine of the Coeur d'Alene district, Idaho,[6] and in the Horn Silver mine, San Francisco region, Utah.[4]

In the Last Chance mine of the Coeur d'Alene district, Idaho, lumps of covellite contain minute specks of chalcopyrite, from which the covellite has been formed as an alteration product.[7] It is abundant in the disseminated copper ores at Bingham, Utah, according to B. S. Butler,[8] and was noted by Boutwell[9] coating chalcopyrite in the Northern Light mine. It forms from chalcopyrite and pyrite in the Rambler mine, Wyoming, and in the Eureka pit, at Copper Flat, Nev.[10] Covellite coats pyrite in the Mountain Monarch prospect, Weaverville quadrangle, California.[11]

According to Lindgren covellite forms a coating on pyrite in sericitized porphyry at Morenci, Ariz.[12] Copper sulphide replaces pyrite also in the Nevada Douglas mine, near Yerington, Nev.[13] At Ducktown, Tenn., covellite covers pyrrhotite.

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[1] Rogers, A. F., A new synthesis and new occurrences of covellite: School of Mines Quart., vol. 32, p. 298, 1911.

[2] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, p. 64, 1911.

[3] Graton, L. C., and Murdoch, Joseph, op. cit., p. 52.

[4] Butler, B. S., The geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 93, 1913.

[5] Graton, L. C., and Murdoch, Joseph, op. cit., p. 51.

[6] Shannon, E. V., Secondary enrichment in the Caledonia mine, Coeur d'Alene district, Idaho: Econ. Geology, vol. 8, p. 569, 1913.

[7] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 92, 1908.

[8] Butler, B. S., U. S. Geol. Survey Mineral Resources, 1912, pt. 1, p. 325, 1913.

[9] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 223, 1905.

[10] Rogers, A. F., op. cit., p. 302.

[11] Ferguson, H. G., Gold lodes of the Weaverville quadrangle, California: U. S. Geol. Survey Bull. 540, p. 44, 1914.

[12] Lindgren, Waldemar, op. cit., p. 186.

[13] Ransome, F. L., The Yerington copper district, Nevada: U. S. Geol. Survey Bull. 380, p. 114, 1909.

As the precipitation of cupric sulphide from cupric sulphate solutions involves no change of valence, some very simple equations may be written:

$$ZnS+CuSO_4=CuS+ZnSO_4.$$
$$CuFeS_2+CuSO_4=2CuS+FeSO_4.$$
$$FeS+CuSO_4=CuS+FeSO_4.$$
$$H_2S+CuSO_4=CuS+H_2SO_4.$$

With pyrite the reaction is probably more involved.

Like chalcocite, covellite is formed in a reducing environment, doubtless in the presence of ferrous sulphate. A paragenesis at Copper Mountain, British Columbia, described by Catherinet,[1] however, suggests the presence of ferric iron. The copper minerals, presumably secondary, were formed in the following order: (1) Bornite, (2) covellite and limonite, (3) chalcocite, (4) chalcopyrite and chalcocite. The hydrous iron oxide appears to have been deposited with covellite between bornite and chalcocite. Limonite forms from ferric rather than from ferrous salt. As copper sulphide is dissolved and not deposited in the presence of ferric salts possibly the iron was deposited from suspension. In this connection the occurrence of considerable finely divided iron oxide suspended in deep waters at Ducktown, Tenn., is suggestive. The mass of evidence seems to indicate that the precipitation of iron oxides along with copper sulphides is not common.

Covellite, like chalcocite, is found in ores of the "Red Beds" of the Southwest, where it was deposited as a primary mineral, presumably from cold solutions. Examples of its deposition by ascending thermal waters are exceedingly rare, but some at Butte, Mont., have been noted above. There it is found at depths below 1,600 feet and in associations which, according to Sales,[2] suggest its deposition by ascending waters. A suite of specimens from the lower levels of the Butte mines, in a collection at the University of Minnesota, shows covellite intergrown with tetrahedrite.

Bornite, Cu_5FeS_4, is found in associations that indicate its formation under many different geologic conditions. It has not been clearly identified as a pyrogenic constituent of an igneous rock, but it is a primary mineral of a pegmatite at Copper Mountain, British Columbia,[3] and it is primary in many contact-metamorphic deposits,

[1] Catherinet, Jules, Copper Mountain, British Columbia: Eng. and Min. Jour., vol. 79, p. 125, 1905. Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 16, 1906.

[2] Sales, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 682, 1910.

[3] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 17, 1906; The rôle of the igneous rocks in the formation of veins: Am. Inst. Min. Eng. Trans., vol. 31, pp. 182–183, 1902.

as at Texada Island, B. C.[1] It occurs in lodes that were formed at great depths. It occurs also in lodes that were formed at moderate depths. It is primary at Virgilina[2] and in the New London mine, near Frederick, Md.[3] It is found also in deposits remote from outcrops of igneous rocks.[4] It is deposited on pyrite and other sulphides by cold copper sulphate waters, and in some deposits it is regarded as an important secondary sulphide. As such it is usually much less abundant than chalcocite. According to Sales[5] it is both primary and secondary at Butte, Mont., where it results from alterations of pyrite, chalcocite, and enargite and is a transition product between pyrite and chalcocite. According to Weed[6] it is in part primary and in part secondary, but it is found mainly above the 1,000-foot level. Sales states that bornite does not often result from the action of downward-moving surface waters but is generally a product of ascending solutions. Graton[7] regards it as a primary mineral in the copper deposits of Shasta County, Cal., in some of which it is found as far as 970 feet below the surface. At Bingham, Utah,[8] bornite is intimately associated with chalcopyrite in the large replacement ore bodies. It is a secondary mineral at Rio Tinto, Spain.[9]

A little bornite was reported from the Vermilion mine, Sudbury district, Ontario, in the early days. As it was not found at depths Coleman[10] regards it as a deposit of surface waters. Bornite was noted by Butler[11] in ores of the Imperial mine, San Francisco region, Utah, but is relatively rare in that region.

Graton and Murdoch[12] state that high-power lenses generally reveal numerous inclusions of other minerals in bornite and attribute to that fact the wide variation of composition shown by chemical analyses. Pure specimens of bornite are not unknown,

[1] Graton, L. C., and Murdoch, Joseph, op. cit., p. 45.

[2] Laney, F. B., The relation of bornite and chalcocite in the copper ores of the Virgilina district of North Carolina and Virginia: Econ. Geology, vol. 6, p. 411, 1911.

[3] Butler, B. S., and McCaskey, H. D., Copper ores of the New London mine: Am. Inst. Min. Eng. Trans., vol. 49, p. 287, 1915.

[4] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 77–78, 1910.

[5] Sales, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 682, 1910.

[6] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 74, 1912.

[7] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, pp. 104–105, 1910. See also Graton, L. C., and Murdoch, Joseph, op. cit., p. 51.

[8] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 106, 1905.

[9] Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, p. 419, 1910.

[10] Coleman, J. P., The nickel industry, with special reference to the Sudbury region, Ontario: Canada Dept. Mines, Mines Branch, p. 26, 1913.

[11] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 95, 1913.

[12] Op. cit., p. 46.

however. Pure isometric crystals from the Bristol mine, Conn., showing well-developed faces, are described by Kraus and Goldsberry.[1] Graton and Murdoch state also that bornite alters very readily under conditions of sulphide enrichment, and where secondary they consider it in general an unstable transition phase formed in the lower part of the zone of sulphide enrichment.

Much remains to be done on the synthesis of bornite. Only by introducing a solid mineral have copper and iron sulphides been simultaneously precipitated in cold solutions, either acid or alkaline. Otherwise all the copper is precipitated first.

Chalcopyrite, $FeCuS_2$, in the greater number of its occurrences is clearly primary, and in many sulphide deposits it is the only important primary copper mineral in the unaltered ore. It is an original constituent of some igneous rocks. It occurs in veins of pegmatite and is abundant in many contact-metamorphic deposits. It is found also in nearly all fissure veins bearing gold, silver, copper, lead, or zinc. A list of occurrences of primary chalcopyrite would include nearly all important deposits of copper ore in the United States. It is, however, a "persistent" mineral, and evidence is rapidly multiplying that it is secondary in many deposits. At Bingham, Utah, according to Boutwell,[2] chalcopyrite is the most important primary copper mineral. It is intimately associated in physical mixtures with pyrite, much of the pyritic ore carrying 3.5 per cent of copper. In the disseminated secondary ores in porphyry a considerable part of the copper is in chalcopyrite. Since it is most abundant in crushed and altered areas, and since it generally occurs along fractures, Boutwell regards it as formed subsequent to the solidification of the porphyry but does not state the nature of the solutions which deposited it. It is a primary constituent of the quartz monzonite at Butte, Mont., and of the copper ores, but according to Weed[3] it is not an important ore mineral at Butte. At Globe it is associated with pyrite in the deeper ores and locally is abundant. It occurs with specularite in the Old Dominion, Gibson, and other mines.[4] No secondary occurrence is mentioned by Ransome.[5] At Bisbee it is in the main but not altogether primary. Some of it is of more recent origin than pyrite. Specimens taken from the periphery of the ore body on the seventh level of the Spray mine, near the inclosing altered and pyritized limestone, show massive chalcopyrite enveloping kernels of pyrite, and veinlets of chalcopyrite

[1] Kraus, E. H., and Goldsberry, J. P., The chemical composition of bornite and its relation to other sulphominerals: Am. Jour. Sci., 4th ser., vol. 37, p. 542, 1914.

[2] Boutwell, J. M., op. cit., p. 106.

[3] Weed, W. H., op. cit., p. 75.

[4] Ransome, F. L., oral communication.

[5] Ransome, F. L., Geology of the Globe Copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, p. 121, 1903.

traverse the pyritic nuclei. Ransome[1] says: "It is necessary to conclude that this particular mass of chalcopyrite was formed after the pyrite and probably in part by alteration or replacement of the latter." According to Kemp,[2] thin films of later chalcopyrite have been found at Butte, Mont., filling crevices between the tabular crystals of covellite, and it is clearly a secondary mineral at Copper Mountain, near Princeton, British Columbia,[3] where it is associated with chalcocite and covellite and is probably later than some of the chalcocite of the ore. In Shasta County, Cal.,[4] it occurs with zinc blende in veinlets cutting the primary ore, and Graton regards it as in part of secondary origin. At Philipsburg, Mont., it occurs sparingly with zinc blende in veinlets which cut the earlier ore. In the veins of Morenci, Ariz.,[5] chalcopyrite is mainly a primary mineral. In a stope of the Ryerson mine it is associated with chalcocite. Of this occurrence Lindgren says: "Such a connection would suggest its origin as due in this case to secondary sulphide formation by solutions from above, for it is known that chalcopyrite, as well as chalcocite, may form under such conditions."

At Cripple Creek, Colo.,[6] chalcopyrite is deposited on tetrahedrite. Chalcopyrite is found as crystals deposited in open spaces in the Cactus[7] ore zone, near Frisco, Utah, and is secondary in the rich ore of the Gossan lead, Virginia.[8] At Ducktown, Tenn.,[9] and in the Rio Tinto mines, Spain,[10] chalcopyrite enrichment below the chalcocite zone has been a process of considerable economic importance.

Of the chemistry of the precipitation of secondary chalcopyrite very little is known. It has not been formed synthetically by cold sulphate solutions in the laboratory. Since it is a sulphide of both copper and iron, and since iron sulphide dissolves in acid, it would be supposed that chalcopyrite would not be precipitated in more than feebly acid solutions, although copper sulphide may be precipitated in solutions more highly acid. In view of these relations it

[1] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 133, 1904.

[2] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 16, 1906.

[3] Catherinet, Jules, Copper Mountain, British Columbia: Eng. and Min. Jour., vol. 79, pp. 125–126, 1905.

[4] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 104, 1910.

[5] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 106, 1905.

[6] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of Cripple Creek, Colo.: U. S. Geol. Survey Prof. Paper 54, p. 121, 1906.

[7] Butler, B. S., op. cit., p. 95.

[8] Weed, W. H., Copper deposits of the Appalachian States: U. S. Geol. Survey Bull. 455, pp. 120–121, 1911.

[9] Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.: U. S. Geol. Survey Bull. 470, p. 151, 1911.

[10] Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, pp. 410–420, 1910.

would be supposed that the precipitation of chalcopyrite would be chiefly below the chalcocite zone. Such relations are suggested by the occurrences of these minerals in some districts, especially at Ducktown, Tenn. But in the laboratory copper and iron sulphides have not been precipitated simultaneously except when other sulphides have been introduced. Chalcopyrite has formed at several hot springs in France on Roman bronze in the presence of hydrogen sulphide or alkaline sulphides.[1]

Chalcopyrite seldom shows crystal boundaries in copper ores, but at an amazingly large number of places it appears in cracks in older sulphides, and in many of these places it appears to have formed from ascending waters. It is to be regarded as one of the later rather than one of the earlier minerals deposited in the course of primary mineralization. Secondary chalcopyrite is formed at the expense of pyrite, bornite, and other minerals, and at Butte it appears to be formed at expense of enargite and covellite.[2] According to Spurr[3] chalcopyrite was found at Monte Cristo, Wash., overlying a crust of hematite, both occupying a crack near the surface.

Cupriferous pyrite is a term formerly often used to describe pyrite which by assays shows the presence of copper but in which no copper mineral is megascopically visible. Microscopic study, particularly the study of polished surfaces, has shown that such ore is generally an intergrowth of pyrite and chalcopyrite, or that the pyrite contains some other copper mineral. According to Simpson[4] a pyrite from Butte, assaying copper, contained chalcopyrite, and all the copper-bearing specimens he examined contained copper minerals. Finlayson[5] showed that the content of Huelva ores also is in copper minerals. On the other hand, cupriferous pyrite from Mount Lyell, Tasmania, according to Gilbert and Pogue,[6] is free from any copper mineral that is visible with the highest objective.

Enargite, Cu_3AsS_4, is a primary mineral of great value at Butte, Mont., is present in considerable amount at Tintic, Utah, and occurs in less abundance at Bingham, Utah, in Gilpin County, Colo., and elsewhere. At Bingham it was found lining druses, showing that it was one of the last minerals deposited, but according to Boutwell[7]

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 659, 1916. Rogers, A. F., Minerals observed on buried Chinese coins of the seventh century: Am. Geologist, vol. 31, p. 46, 1903.

[2] Sales, R. H., Superficial alteration of the Buttee veins: Econ. Geology, vol. 5, p. 15, 1910.

[3] Spurr, J. E., Geology and ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 838, 1901.

[4] Simpson, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, p. 628, 1908.

[5] Finlayson, A. M., op. cit., p. 420, 1910.

[6] Gilbert, C. G., and Pogue, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., vol. 45, p. 619, 1913.

[7] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 108, 1905.

there is no conclusive evidence that it was deposited by sulphate waters.

Enargite replaces orthoclase phenocrysts in a porphyry at Summit district, Colo.,[1] and is found also in the Red Mountain district[2] near Ouray.

The enargite of Butte, according to Emmons and Tower, is primary.[3] Weed[4] observes that some of it was deposited, however, by hot ascending solutions after the earlier chalcopyrite veins had formed. Both Reno Sales[5] and A. N. Winchell[6] regard enargite at Butte as mainly primary.

J. C. Ray found enargite partly replacing pyrite and quartz in ores from deep levels at Butte, Mont.[7] Enargite is found also in the upper portions of veins above the water level at Butte and at Tintic, but in view of its great insolubility[8] in sulphuric acid waters it is probably residual. Little conclusive paragenetic evidence is available that it is deposited by descending sulphate waters. At Butte it is intergrown with chalcocite, but as stated above some of the chalcocite of the Butte deposits is primary.

At Bor, Serbia, according to Lazarevic, enargite is both primary and secondary. Some of the enargite occurs in baritic veins and some with pyrite and covellite in cavities. It has been stated by Lazarevic[9] that covellite is generally present in enargite deposits. There are a great many deposits with covellite, however, in which there is no enargite. Crystals of enargite at Butte[10] are partly converted to bornite and chalcopyrite.

Famatinite, Cu_3SbS_4, is not a common ore of copper, and little is known as to its origin. I know of no occurrence that is secondary. In view of the primary origin of enargite, its corresponding arsenic salt, famatinite also is probably of primary origin.

Tetrahedrite, $Cu_8Sb_2S_7$, is a comparatively common copper mineral. In most of its occurrences it is of primary origin. Its genesis is discussed on page 278.

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[1] Pirsson, L. V., On the crystallization of enargite: Am. Jour. Sci., 3d ser., vol. 47, p. 214, 1894.

[2] Thornton, W. M., jr., An association of enargite, covellite, and pyrite from Ouray County, Colo.: Am. Jour. Sci., 4th ser., vol. 27, p. 358, 1910.

[3] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[4] Weed, W. H., Ore deposition and vein enrichment by ascending hot waters: Am. Inst. Min. Eng. Trans., vol. 33, p. 748, 1903.

[5] Sales, R. H., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 681, 1910.

[6] Winchell, A. N., idem, p. 488.

[7] Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, p. 470, 1914.

[8] Buehler, H. A., and Gottschalk, V. H., Oxidation of sulphides: Econ. Geology, vol. 5, p. 31, 1910.

[9] Lazarevic, M., Die Enargit-Covellin-Lagerstätte von Cuka-Dulkan bei Bor in Ost-Serbien: Zeitschr. prakt. Geologie, vol. 20, p. 337, 1912.

[10] Graton, L. C., and Murdoch, Joseph, op. cit., p. 60.

Tennantite, $Cu_8As_2S_7$, is the arsenic salt corresponding to tetrahedrite, but it is not so common as tetrahedrite. Its genesis is discussed on page 280.

COPPER-BEARING DEPOSITS.

BUTTE, MONTANA.

The Butte district,[1] in western Montana, is an area of quartz monzonite (the Butte quartz monzonite, frequently called granite), which is intruded by a later aplite, or aplitic granite (in early reports sometimes alluded to as the "Bluebird granite"), and by rhyolite porphyry (in early reports called quartz porphyry).

Dikes of late Tertiary rhyolite cut the granite, and effusive rhyolite (rhyolite dacite) rests upon it. In the western part of the region are Tertiary lake beds more recent than the granitic rocks. These are composed of sand, gravel, and water-laid tuff. The rhyolite porphyry has in some reports been referred to as the "Modoc porphyry," and it is locally known by that name. In Weed's most recent publication on this area[2] it is called rhyolite porphyry. Its groundmass is microcrystalline, however, and, as Weed very truly states, it might be classed as granite porphyry.

The quartz monzonite, aplite, and porphyry, which contain all the ores, are phases of the great Boulder batholith, which extends some 64 miles southward from a point near Helena and is 12 to 16 miles wide. This batholith intrudes Paleozoic and Cretaceous sedimentary rocks and along its borders has induced contact metamorphism by which the typical garnet zones have been developed in the calcareous sediments. There are, however, no metamorphosed sediments in the Butte mining district.

Although the rocks of the batholith are in general of comparatively uniform composition, the Butte quartz monzonite is a somewhat more basic phase. The aplite represents a differentiation product that was forced into cracks in the quartz monzonite after that rock had cooled. Although there is an unusual amount of the aplite in the region about Butte, its economic significance is not clear. Indeed, the lodes, on passing from the quartz monzonite into aplite, are im-

[1] Weed, W. H., Emmons, S. F., and Tower, G. W., jr., U. S. Geol. Survey Geol. Atlas, Butte folio (No. 38), 1897. Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, 1912. Winchell, H. V., Synthesis of chalcocite and its genesis at Butte, Mont.: Eng. and Min. Jour., vol. 75, pp. 782–784, 1903. Sales, R. H., Ore shoots at Butte, Mont.: Econ. Geology, vol. 3, pp. 326–331, 1908; Superficial alteration of the Butte veins: Idem, vol. 5, pp. 15–21, 1910; Ore deposits of Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 40, pp. 3–106, 1914. Simpson, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, pp. 628–636, 1908. Kirk, C. T., Conditions of mineralization in the copper veins at Butte, Mont.: Econ. Geology, vol. 7, pp. 35–82, 1912. Ray, J. C., Paragenesis of the ore minerals in the Butte district, Montana: Econ. Geology, vol. 9, pp. 463–481, 1914. Linforth, F. A., Applied geology in the Butte mines: Am. Inst. Min. Eng. Trans., vol. 46, pp. 110–127, 1914. Bard, D. C., and Gidel, M. H., Mineral associations at Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 46, pp. 123–127, 1914.

[2] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 41, 1912.

poverished, and Weed[1] states that the aplite is uncongenial for ore deposition because it fractures with difficulty and is not readily replaced.

There seems to be a genetic relationship between the copper ores and the porphyry intrusives, although such relation is not conclusively proved. The porphyry is found mainly in the eastern portion of the copper area, where it is younger than the Butte quartz monzonite and older than the veins, since even the oldest veins cut through it. The veins in the porphyry, like those in the aplite, are narrower and poorer than those in the quartz monzonite. The porphyry is, however, the youngest igneous rock exposed that is older than the oldest veins.

The copper ores are included in an area about 1½ miles long and a mile wide, and this area is almost surrounded by a much larger area containing closely spaced silver-bearing veins. Pronounced parallelism is noticeable in veins of both groups.

The fissuring in the district is exceedingly complex. The systems as outlined by R. H. Sales[2] are (1) Anaconda system; (2) Blue system of fault fissures; (3) Mountain View breccia faults; (4) Steward system; (5) Rarus fault; (6) Middle faults; (7) Continental fault.

1. The Anaconda system is composed of east-west fissures which are generally heavily mineralized and along which there has been but little displacement. In general they dip south at high angles. In the copper-producing area there are two important groups of veins belonging to the Anaconda system. On the south, or Anaconda group, are located the deposits of the Gagnon, Original, Parrot, Never Sweat, Anaconda, St. Lawrence, Mountain View, Leonard, West Colusa, and other mines. North of this group and separated from it by a comparatively barren area, is the second group which includes the Syndicate, Bell, Speculator, and associated fissures. Joining some of the east-west fractures are many smaller fractures closely spaced and doubtless of the same age. They strike about N. 20° W. and thus join the east-west fissures at large angles. Many of them play out toward the southeast or join other fractures. They form altogether a network with what Sales has designated "horsetail" structure. In some mines the most important ore bodies are along these northwest conjugated fractures. They are well developed in the Tramway, Leonard, and West Colusa mines, where large ore bodies are stoped from them. North of the copper-bearing area are the great silver and zinc east-west lodes. These also are believed to belong to the Anaconda system of fissures.

[1] Weed, W. H., op. cit., p. 96.

[2] Sales, R. H., Ore deposits of Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 46, p. 12, 1914.

2. The Blue system is composed of several fissures that strike northwest. These cross and fault the veins of the Anaconda system. Members of the Blue system include the Clear Grit, Blue, Diamond, High Ore, South Bell, Skyrme, Edith May, and other veins. These veins are spaced with considerable regularity and show regular strike lines, although they differ greatly as to dip. The prevailing dip is, however, to the southwest. These fissures are faults, many of them having displacements of 150 to 300 feet. The grooves in the fault planes are generally rather flat-lying, and the displacements are nearly horizontal shifts to the northwest on the northeast sides of the fault fissures. Although the movements of the hanging walls have downward components as well as horizontal components, owing to the larger amount of horizontal movement, the faults appear on the plans as "reverse" faults. The lodes of the northwest, or Blue vein system, carry large deposits although they are much less important than lodes of the east-west fractures. They are, moreover, less uniformly mineralized than the east-west veins on which the deposits are almost continuous except where displaced by faults.

3. The Mountain View breccia faults, which are notably developed in the Mountain View, Leonard, and Gagnon mines, are persistent fissures filled with angular or rounded fragments of country rock and of earlier veins. They strike about N. 75° E. Near veins they contain locally enough brecciated ore to be worked. They are later than the deposits of the Blue vein system.

4. The Steward system includes fault fissures that strike about N. 65° E., dip about 65° S., and extend across the Butte district. They include the Rob Roy, Mollie Murphy, Steward, Modoc, and Poser fissures. The Steward fissures are in general planes of movement. Displacements range from 50 feet or less to 150 feet. As a rule the hanging wall moved downward in these faults along a direction 70° with the horizontal. They rarely carry ore.

5. The Rarus fault is a complex fissure that is later than the Anaconda, Blue, and Mountain View systems of fractures and veins. It is known also to be later than some of the veins of the Steward system. It strikes northeastward and dips 45° NW. It is a broad crushed zone from 20 to 250 feet wide, and is limited by tabular masses of fault gouge from 1 to 8 inches wide. The displacement is not uniform. In the northeast part of the district it is very slight, while in the southwest part it is as much as 350 feet. The hanging wall at some places moved downward on the dip, but in the Leonard mine the movement was 60° with the horizontal or less. The ore in the Rarus fault, thus far developed, is drag ore from older veins.

6. The Middle faults, as developed in the Mountain View mines, represent a period of movement later than the Rarus. They are not mineralized.

7. The Continental fault, which is on the east edge of the mineralized area, is likewise later than the metallization of the district.

The relations of the fracture systems to each other are stated above. The earliest or east-west fracturing followed the consolidation of the aplite and of the quartz porphyry. The volcanic outbreak which caused the rhyolitic intrusion occurred subsequent to the earlier vein fissuring; the silver veins are cut off, in places cut in two, by intrusive dikes of rhyolite. The relation of these rhyolite dikes to the different periods of late fracturing is, however, not positively known. The rhyolite dikes themselves have been markedly sheeted and somewhat fractured since their intrusion. The rhyolite intrusion, however, was probably accompanied by a certain amount of fracturing of the adjoining rocks. It is therefore not improbable that the secondary fracturing, which had an important bearing on the enrichment of the copper veins, was genetically connected with the intrusion of the rhyolite.

Hydrothermal alteration of the quartz monzonite is extensive. Where large veins are closely spaced the entire area of quartz monzonite is hydrothermally altered; where the veins are less closely spaced fresh rock is found between them. Kirk[1] recognizes two phases of alteration; an earlier chloritic phase, followed by a later sericitic phase. The veins are replacement deposits, and, according to Sales, 60 to 80 per cent of the ore is altered quartz monzonite with disseminated sulphides.

The ores are of three distinct classes—copper, siliceous silver, and zinc. The copper ores contain a little silver; the silver ores rarely contain much copper; both copper and silver ores contain a little gold, and the high-grade silver ores contain it in notable amounts.

Chalcocite, enargite, and bornite are the most common copper minerals. Covellite occurs in large amounts in the Leonard mine and in small amounts in others. Chalcopyrite is present in workable quantities in a few properties but is an insignificant part of the total copper ore output. Tetrahedrite is found in the deep workings of a few mines. Chalcanthite is common in the old workings. Pyrite is the most common sulphide. It is estimated by Weed that since the beginning of mining about 75 per cent of the copper production has come from glance, 20 per cent from enargite, 4 per cent from bornite, 0.5 per cent from covellite, 0.5 per cent from chalcopyrite.

Silver occurs native in the copper ores, especially in those from the upper levels. Ruby silver and indeterminable black sulph-

[1] Kirk, C. T., op. cit., p. 38.

antimonites and sulpharsenides occur in the siliceous silver ores. Free gold is rare but occurs in some silver ores and has been seen in specimens from the Leonard mine, where it is parasitic on glance. The gangue minerals include quartz, sericite, and several residual minerals of the altered country rock. Rhodonite and rhodochrosite occur in silver and zinc ores.

Sales states that there is a "central zone" of copper ore, mainly chalcocite and enargite, which grades into an "intermediate zone" which contains ores with the same minerals, and in addition to them sphalerite, rhodochrosite, and rhodonite, with a slight increase of silver content. In an outer or peripheral zone the ores carry sphalerite, rhodonite, rhodochrosite, tetrahedrite, tennantite, and chalcopyrite, but rarely chalcocite or bornite. Their chief metals are silver, gold, zinc, and some lead.

The mountains near by have been glaciated in recent geologic time, but no morainal material is found in the immediate vicinity of Butte.[1] The average precipitation is less than 20 inches, but the loose disintegrated material near the surface favors extensive seepage of rain water. The few records of "first water" for the older mines appear to locate it at about the upper limit of the sulphide ores. This upper limit differs greatly, ranging from about 20 feet to 400 feet, being in part independent of the surface level but differing with the degree of fracturing.

In the quartz monzonite the network of lesser fractures and the veins and faults are apparently all filled with water and serve as a vast reservoir. That this water has a natural level not far below that of the neighboring valleys is evident, and that it is moving slowly downward can not be doubted, though it can not be readily proved. The conditions of mineralization afford some evidence of this; and in the East Ridge region, where higher collecting ground exists, the springs became dry when the Altona mine was pumped out to a depth of some 200 feet, proving a connection between the mine waters and surface drainage. The drying out of the upper workings of some of the mines when the surface seepage is eliminated shows that in these mines the waters come from above. In short, all the evidence shows that the waters are surface waters seeping downward. They come, however, from a broad area, and not from the surface of the Butte mines alone.[2]

In opening new ground the amount of water, as stated by Weed, seems to be proportionate to the block of ground opened—that is, the ground between the new level and the old workings above. In a few places rising water was encountered at the deep levels—for instance, on the 2,200-foot level of the Mountain Con mine and on

[1] Weed, W. H., op. cit., p. 80. [2] Idem, p. 98.

the 1,600-foot crosscut of the Anaconda (where uprising waters were encountered some 2,000 feet from other workings)—but the outflow diminished in a few weeks and finally all but ceased, indicating that the area from which the water came was probably drained.[1]

The oldest mineralized fissures, including the Parrot, Anaconda, and Syndicate, occupy openings along which there was but slight tangential movement.[2] They have been fractured, however, since the ore was deposited. The ore minerals in these veins consist chiefly of pyrite, chalcopyrite, chalcocite, covellite, etc. According to Sales they contain some enargite also. Pyrrhotite is unknown in these and in all other deposits of the district. Sphalerite is abundant in some of the copper veins and wanting in others. These veins are locally enriched at great depths.

The Blue system of fissures strikes northwest across the east-west veins. These contain, in addition to the minerals named as constituents of the earlier veins, large quantities of enargite. Along these veins evidence of movement parallel to the planes of the deposits is pronounced. Although mineral composition of the veins is comparatively uniform, the later fissures are characterized by barren patches separating rich ore shoots. These ore shoots, as shown by Sales,[3] are of primary origin, the course of the mineralizing solutions having been determined by fault gouge, which effectively dammed back the waters from the portions of the fissures that are barren.

Some silver lodes outcrop conspicuously. The outcrops of copper lodes are not prominent. The leached zone extends downward in places 300 or 400 feet below the surface. It contains some silver, locally 30 ounces or more per ton, but little copper. Below the oxidized zones of copper lodes, grading into them locally within 2 or 3 feet, are enormous masses of chalcocite, with some bornite and covellite. This ore carries in general 2 or 3 ounces of silver per ton.

In the great ore bodies of the upper levels of the Anaconda veins chalcocite occurred, according to Weed,[4] in masses of nearly pure leadlike mineral 20 feet or more wide. In depth the mineral shows a more crystalline structure, and it is found in all the mines in greater or less abundance and purity, but in the great bulk of the ores it forms small grains scattered through the ores.

Emmons, Weed, Tower, and many others who studied the copper lodes in the earlier stages of their development regarded the chalcocite ores as secondary deposits formed by descending waters.

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[1] Weed, W. H., op. cit., p. 97.
[2] Sales, R. H., Ore shoots at Butte, Mont.: Econ. Geology, vol. 3, p. 327, 1908.
[3] Idem, p. 326.
[4] Weed, W. H., The copper mines of the world, p. 327, New York, 1907.

C. T. Kirk,[1] after a comprehensive study of the ores of the Pittsmont mine of this district, concluded that the chalcocite was secondary, basing his argument in part on its association with kaolin.

As a result of microscopic studies of polished surfaces of ores, John F. Simpson[2] concluded that the copper sulphides were deposited in the following order: Chalcopyrite, enargite, bornite, chalcocite. Pyrite from the 2,000-foot level of the Mountain Con mine is cut by veinlets of bornite and contains flakes of chalcocite. In ore from the 800-foot level of the Alex Scott mine chalcocite surrounds pyrite, enargite, and chalcopyrite and occurs as veins in the pyrite. As the underground workings have been carried deeper, and as chalcocite ores have been developed in depth, doubt has been expressed more and more as to the validity of the conclusions that the chalcocite ores are wholly secondary.

In Weed's most recent report on the district[3] he states that the bulk of the ore is altered quartz monzonite containing disseminated grains and veinlets of chalcocite intergrown with pyrite or replacing that mineral completely. He also notes that chalcopyrite is but sparingly developed, constituting but 0.5 per cent of the ore mined. The copper of the secondary ore must therefore have been derived in the main from enargite, cupriferous pyrite, or older chalcocite.

A drawing by Bard[4] shows an inch vein of chalcocite cutting quartz. The chalcocite incloses idiomorphic crystals of pyrite and quartz, and both of these minerals seem to be spaced with some regularity in the chalcocite.

An additional observation supporting the theory that the chalcocite is largely primary is its great abundance compared with other copper minerals. The small amount of chalcopyrite and bornite in the deeper ores of the Anaconda system appears to be inadequate as a source of primary copper. Lately Sales has discussed the origin of the chalcocite ores in considerable detail. He believes that the sooty chalcocite is mainly secondary, though some has formed from primary chalcocite. The massive chalcocite he considers primary. The conclusion that much of the chalcocite is primary is thus supported by several lines of evidence. It should be noted here, however, that massive secondary chalcocite is not rare, and that H. V. Winchell, in his experiments on the synthesis of chalcocite (p. 165), obtained glistening coatings, not the dark powder.

[1] Kirk, C. T., Conditions of mineralization in the copper veins at Butte, Mont.: Econ. Geology, vol. 7, p. 35, 1912.

[2] Simpson, J. F., The relation of copper to pyrite in the lean copper ores of Butte, Mont.: Econ. Geology, vol. 3, p. 635, 1908.

[3] Weed, W. H., Geology and ore deposits of the Butte district, Mont.: U. S. Geol. Survey Prof. Paper 74, p. 76, 1912.

[4] Idem, p. 76. The original is not available to me.

Briefly stated the secondary copper ore is believed by all to be an important feature of the east-west or Anaconda lode system, but it is less important in the northwest Blue vein system. In the Mountain View mine the sooty chalcocite is from 800 to 1,200 feet deep, according to Sales, and in the Mountain Con, according to Weed, secondary chalcocite was forming at the 2,000-foot level when the latter was opened.

We have mentioned already the "disseminated ores in porphyry," which are so extensively developed in Utah, Nevada, and New Mexico. Much of the ore at Butte is "disseminated" in the granite, but the deposits are more closely restricted to the veins and generally extend to greater depths than in the districts named above. On the east edge of the Butte district, however, in the region of the Continental fault, on the Bullwhacker, Butte & Duluth, and adjoining properties, oxidized copper minerals are disseminated in crushed and altered granite that carries 1.4 to 4 per cent copper. The unoxidized granite carries copper in small amounts[1] and this has apparently been concentrated by weathering.

BINGHAM, UTAH.

The Bingham district, Utah,[2] is an area of Carboniferous quartzites and limestones intruded by monzonite and monzonitic porphyry and covered in part by andesites, andesitic porphyries, and breccias. The rocks are tilted, faulted, and in places highly shattered. The ore deposits are in or near the intrusive monzonite or monzonitic porphyry. They include fissure veins in several formations, bedding-plane deposits in limestones, and disseminated deposits in shattered porphyry. The ore bodies that until recently have been most productive are large replacement deposits of sulphide ore in limestone. These ores consist chiefly of pyrite, chalcopyrite, sphalerite, and chalcocite, with a little bornite and enargite and their oxidation products. In many of the deposits a little pyrrhotite is present, and in some ore from the Highland Boy mine pyrrhotite is more abundant than chalcopyrite.[3]

In some of the mines oxidation is deep, extending to depths several hundred feet below the surface. In the Brooklyn mine[4] oxidation is reported to a depth 1,450 feet below the surface; in the Highland Boy it is only 300 feet deep. In some of the deposits chalcocite ores extend to considerable depths and in others they are sub-

[1] Sales, R. H., The ore deposits at Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 46, p. 41, 1914.

[2] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, 1905.

[3] Idem, p. 105.

[4] Idem, p. 215.

ordinate. The chalcocite zone in the Highland Boy seems not to have been extensive. Boutwell notes that the secondary oxidized ores of copper and gold pass into a zone characterized by chalcopyrite tarnished and coated with bornite and seamed with limonite. A winze sunk through oxidized ore encountered gold in considerable quantities, some of the ore running over $30 to the ton. Five thousand tons of ore shipped early in the development of this mine is said to have averaged 12 per cent copper and $4 gold to the ton and to have contained much silver. It is reported also that the valuable metals in each of the three principal ore bodies ran higher in the upper than in the lower levels. The ores of the lower levels carried pyrite, pyrrhotite, chalcopyrite, considerable gold, and some silver. In 1906 and 1907, according to Graton,[1] practically all the copper from these deposits was derived from the pyritic ore.

Another type of ore deposit which in recent years has become highly productive contains copper ore disseminated in the monzonite porphyry. The principal deposit of disseminated ore is in the intrusive body at Upper Bingham known as the Bingham laccolith. According to Boutwell,[2] this extensive mass of monzonite porphyry carries disseminated throughout its areal extent, so far as known, irregular grains of pyrite and chalcopyrite. The mineralized tract contains a multitude of thin unsystematized parting planes. The rock is greatly bleached, silicified, and sericitized in and near the areas of great shattering. The copper content is lowest in the oxidized zone at the surface. Farther down, in the unoxidized rock, the copper ore lies in flat scales and films in silicified walls of cracks, and in areas of great shattering it occurs abundantly on quartz-coated cracks and is disseminated through the silicified bleached walls. The quartz, sericite, brown mica, and some orthoclase[3] in this ore are later than the original rock-making minerals. I can find no record of the occurrence of pyrrhotite in these ores. Zinc blende is not mentioned in Boutwell's description of this deposit, although it is abundant in some of the lode ores in the monzonite—for example, in that of the Last Chance mine.[4] Although some of the metals may have been present in the rock when it solidified,[5] the larger part of the primary sulphides was introduced by thermal waters after the porphyry had solidified.

Of the surface alteration of disseminated ores Boutwell[5] says:

Superficial alteration has followed the deposition of chalcopyrite and pyrite. Pyrite about its periphery and along cracks which traverse these planes may be

[1] Graton, L. C., U. S. Geol. Survey Mineral Resources, 1906, p. 404, 1907; idem, 1907, pt. 1, p. 615, 1908.
[2] Boutwell, J. M., op. cit., p. 167.
[3] Butler, B. S., U. S. Geol. Survey Mineral Resources, 1912, pt. 1, p. 325, 1913.
[4] Boutwell, J. M., op. cit., pp. 160, 178.
[5] Idem, p. 172.

seen going over to limonite. This fact * * * doubtless explains the relative enrichment of gold values proved by assays to exist in the outer surface portions of test tunnels in these copper and gold bearing intrusives. The brilliant tarnish of grains of chalcopyrite indicates a beginning of alteration, and thin rims of a dark grayish-black metal about chalcopyrite observed under the microscope suggest continuance of that process and replacement by black copper sulphide. Rims of a blue-black metallic sulphide occur around grains of chalcopyrite. The reason for the decrease in assay values of copper along certain open and water-bearing fracture zones is doubtless to be found in the well-known fact that under the action of surface waters copper suffers rapid alteration and transportation.

It appears, then, that in the disseminated ores in igneous rock the copper minerals were deposited by hydrothermal action subsequent to the date of igneous intrusion, and that these sulphides are now undergoing normal superficial alteration.

The Utah Copper Co., which is exploiting the ores of the Bingham laccolith, is said to have developed about 338,000,000 tons, the average content of which is about 1.5 per cent copper and from 20 to 30 cents a ton in gold and silver. The surface of this ore body occupies an area of 217 acres, and the average thickness of the workable ore is probably about 424 feet.

The leached capping, which is stripped by steam shovels, has an average thickness for the entire area of 110 feet. The average depth of the bottom of the deposit now workable is 520 feet below the surface, although it extends downward in places more than 900 feet below the surface.[1] In much of the ore zone, especially in ore of lower levels, considerable masses of the ore carry comparatively little chalcocite. As stated by Butler,[2] chalcopyrite and covellite are important ore minerals. It is not known whether the chalcopyrite is a primary or secondary sulphide.

In 1911 the Utah Copper Co. produced from copper ore about a million dollars in precious metals, four-fifths of which was gold and about one-fifth silver. This is equivalent to about $0.225 per ton of ore and 1.07 cents per pound of copper. It is said that gold is concentrated in the oxidized zone, but below that zone it tends to increase or decrease with the copper content of the sulphide ore.

BISBEE, ARIZONA.

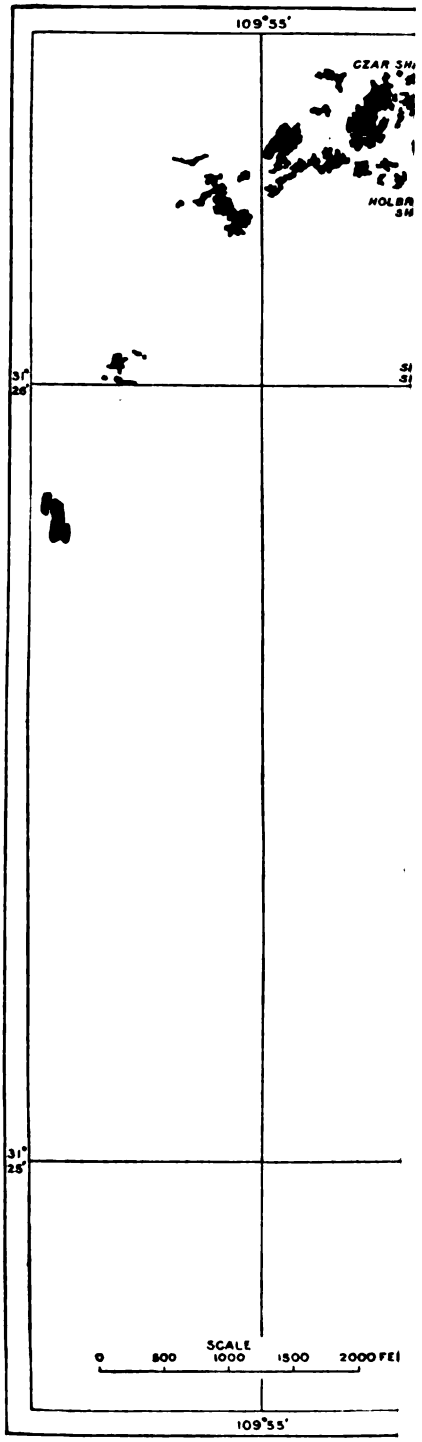
The geology of the Bisbee (Warren) district, Arizona, was studied in detail about 12 years ago by Ransome.[3] Since the publication of his report the known productive area has been much extended, and large new mines have been developed, especially in a part of the district to whose economic possibilities this report specifically directed

[1] See cross section, Utah Copper Co. Seventh Ann. Rept., for 1911.

[2] Butler, B. S., op. cit., p. 324.

[3] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, 1904; U. S. Geol. Survey Geol. Atlas, Bisbee folio (No. 112), 1904.

U. S. GEOLOGICAL SURVEY



HORIZONTAL PROJECTION OF

attention. In view of these later developments Mr. Ransome, who revisited Bisbee in 1912, has kindly prepared the following note, in which is presented more recently acquired information than could have been included in a mere abstract of published work. Plate VII and figure 15 indicate the extent of mining operations in the Bisbee district.

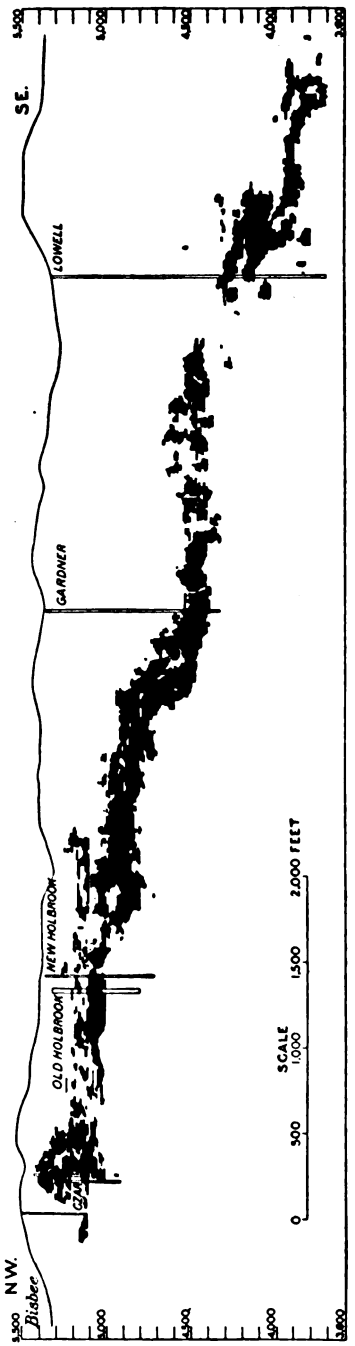


FIGURE 15.—Generalized vertical projection of stoped ore bodies in the Warren district, Bisbee, Ariz., Jan. 1, 1912. After F. L. Ransome.

NOTE ON THE BISBEE DISTRICT, ARIZONA.

By F. L. RANSOME.

The fundamental rocks of the Bisbee district are the pre-Cambrian Pinal schist and probably also the granite mass of Juniper Flat, north of Bisbee, which is intrusive into the schist. Although the age of this granite is not directly evident from its geologic relations and although in Professional Paper 21 and in the Bisbee folio it was regarded provisionally as Mesozoic, the texture and character of the rock, in the light of subsequent experience in Arizona, suggest pre-Cambrian age. There rests on the schist in successive upward sequence (1) the Bolsa quartzite (Cambrian), 430 feet thick; (2) the Abrigo limestone (Cambrian), 770 feet thick; (3) the Martin limestone (Devonian), 325 feet thick; (4) the Escabrosa limestone (Mississippian, "Lower Carboniferous"), 700 feet thick; and (5) the Naco limestone (Pennsylvanian, "Upper Carboniferous"), 3,000 feet or more thick. These beds were intruded in early Mesozoic time by stocks, dikes, and sills of granite porphyry and, after deep ero-

sion, were covered by a thick series of Cretaceous (Comanche) beds. These have in greater part been eroded away from the productive area of the district.

Structurally the district is characterized by numerous faults, some older and some younger than the Cretaceous beds. In some of the tilted fault blocks the strata are gently folded, but folding is a much less conspicuous feature of the structure than faulting.

The primary ores were deposited during or after the intrusion of the granite porphyry and before the deposition of the Cretaceous beds. Their age is therefore early Mesozoic. Their deposition was connected with a decided but not conspicuous contact metamorphism of the limestones, shown by the development within these of tremolite, diopside, garnet, and other silicates, generally in crystals of microscopic size. The ore bodies that first gave prominence to Bisbee are those in the Carboniferous and Devonian limestones, but recent developments are bringing to light important lenticular masses of ore in the Cambrian limestone, and a little ore has been found in the porphyry.

Very briefly stated, the larger structural features to which the occurrence of the ores is related are (1) the northwest-southeast Dividend fault, which has a normal throw that has brought Paleozoic beds on the southwest side of the fissure against Pinal schist on the northeast side; (2) a small stock of granite porphyry intruded on the line of the fault and invading the contiguous schist and Paleozoic beds; (3) an open synclinal structure in the down-faulted Paleozoic beds, which is such that these dip in part toward the porphyry stock and in conjunction with the fault plane form a trough pitching to the southeast; and (4) a gentle tilt to the southeast, as shown by the present slope of the pre-Comanche erosion surface. The ore bodies occur in the down-faulted fragment of a syncline, are disposed in roughly semicircular fashion around the porphyry stock, and have radial prolongations along certain zones of fissuring.

Though very irregular in form, the ore masses as a rule are roughly lenticular and tend to conform with the bedding of the limestones. The average thickness of all the ore bodies has been calculated by the engineers of the Copper Queen Co. to be about 33 feet. The shape and position of many of the bodies, however, are determined by zones of fissuring and by the form of intruded porphyry masses, many of which do not extend directly upward to the surface. With possibly a few relatively unimportant exceptions, the known Bisbee ore bodies were originally deposited as metasomatic replacements of the limestones. In many of the ore bodies in the Abrigo limestone the positions of former bedding planes are clearly shown by a banding in the ore.

At the Copper Queen mine, near the northwest end of the structural trough, the ore bodies came to the surface. As development was pushed south and east, around and beyond the exposed porphyry mass of Sacramento Hill, through the Holbrook, Spray, Irish Mag, Gardner, Oliver, Lowell, Hoatson, and Junction shafts, the ore was found at greater depths. The great ore body of the Junction mine of the Calumet & Arizona Co., south of Sacramento Hill, whose existence was unknown when Professional Paper 21 was written, extends from a point 10 feet above the 1,300-foot level to the 1,500-foot level. It is 500 feet long and from 10 to 120 feet wide in plan, part of this width being due to duplication by faulting. South of the curved chain of mines mentioned lie the Briggs and other important ore bodies connected with zones of north-northeast and south-southwest fissuring in the limestone. In the Briggs mine the ore bodies grade outward into a huge, partly oxidized mass of pyrite about 1,500 feet long and in places 800 feet wide.

In the Copper Queen, Lowell, and Hoatson mines the ore bodies are, as a rule, confined to the vicinity of intrusive masses of porphyry. In the Junction mine the connection between ore and porphyry is less close, and in the Briggs mine no porphyry is known. Apparently the bodies of porphyry, like the fissures in the limestones, played an important part in controlling the movements of the ore-bearing solutions, but it is not believed that any considerable part of the ore constituents came from the porphyry masses now visible; the metallic elements and sulphur had a more distant source.

Up to the year 1904 nearly all the copper obtained at Bisbee came from oxidized or enriched ore. Of late years, however, primary ores have become very important. The Junction ore body, in which the present stopes average over 9 per cent of copper, is a nearly solid mass of sulphides that are mostly primary. The huge pyritic mass of the Briggs mine, with its included bodies of more cupriferous material, is largely primary, and the ore lenses in the Abrigo limestone have, as a rule, undergone no enrichment.

The most abundant sulphides in the primary ore are pyrite and chalcopyrite. With these may be associated considerable bornite and in certain ore bodies magnetite. Of late years both sphalerite and galena have been found in considerable quantity near the porphyry of Sacramento Hill, but these minerals are not widely distributed in the copper ores. No pyrrhotite has been noted.

The altitude of this district ranges from 5,000 to 7,400 feet above the sea. The average rainfall is about 17 inches and the surface of the ground water as a rule lies deep. Water was reached in the Lowell mine at a depth of 1,100 feet. Afterward the Junction shaft, 1,800 feet deep, drained the Lowell. For a time, when the lower Junction levels were kept open, the pumps raised over 6,000,000 gallons in 24 hours.

The natural ground-water surface and the lower limit of oxidation are neither coincident nor parallel. In general in the northern part of the productive area much enriched sulphide ore lies above the original water level, and in the southern part there is considerable oxidized material below it. In the Junction mine, for example, there is oxidized and leached material on the 1,500-foot level (corresponding to a depth of 1,750 feet in the Lowell shaft), and oxidized ore is mined in places on the 1,600-foot (bottom) level of the Lowell mine. The lower depth of oxidation ranges from 200 feet to at least 1,600 feet.

Although the relative importance of the enriched chalcocitic ores at Bisbee has been diminished by the discovery of large bodies of profitable primary ore, they still supply a large proportion of the total copper produced. The lower limit of enrichment is irregular and ill-defined but, like the lower limit of oxidation, is deeper in the southern part of the productive area than in the northern part. Secondary chalcocite occurs in the bottom level of the Lowell mine (1,600 feet) and on the 1,300-foot level (1,400 feet deep) of the Briggs mine. How much deeper it may go is not known. In some places sulphide enrichment has worked down to the bottom of a pyritic ore body; in others it has worked around and under residual masses of unenriched pyritic material; and in parts of the Briggs mine large masses of leached and oxidized material rest directly on unenriched, low-grade pyrite. The enriching mineral is generally chalcocite. In some loose, friable ore the chalcocite may occur as thin shells around grains of pyrite and as a sooty interstitial powder. Elsewhere the replacement is more nearly complete, the original chalcopyrite and much or all of the pyrite having been converted into massive chalcocite. Secondary chalcopyrite has been noted,[1] but the greater part of this mineral is probably a primary constituent of the Bisbee ores.

The great depths to which oxidation and enrichment have penetrated at Bisbee and the inclined position of these zones of alteration with reference to the present underground water level and their approximate parallelism with the old pre-Comanche erosion surface indicate that much of the oxidation and enrichment were effected before the deposition of the Cretaceous formations.

GLOBE AND MIAMI DISTRICTS, ARIZONA.

For the following note also I am indebted to Mr. Ransome, who studied the Globe district[2] some years ago and who is now investigating the Miami copper deposits.

[1] Ransome, F. L., The geology and ore deposits of the Bisbee quadrangle, Arizona: U. S. Geol. Survey Prof. Paper 21, p. 132, 1904.

[2] Ransome, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, 1903; U. S. Geol. Survey Geol. Atlas, Globe folio (No. 111), 1904.

THE GLOBE AND MIAMI DISTRICTS, ARIZONA.

By F. L. Ransome.

In the Globe quadrangle, which includes the Miami district, a pre-Cambrian crystalline complex, consisting of Pinal schist and various granitic intrusives ranging from quartz diorite to true granite, is unconformably overlain by a thick series of Cambrian and perhaps pre-Cambrian beds. The stratigraphic column as revised after recent work in the adjoining Ray quadrangle is as follows:

Pre-Mesozoic stratigraphic column in the Globe region, Arizona.

		Feet.
Erosion surface.		
8. Tornado limestone (Carboniferous)		1,000
7. Martin limestone (Devonian)		325
6. Troy quartzite	Cambrian or older	400
5. Mescal limestone		250
4. Dripping Spring quartzite		450
3. Barnes conglomerate		10–55
2. Pioneer shale		200
1. Scanlan conglomerate		1–6

These rocks were extensively intruded, probably during the Mesozoic, by diabase, largely as great irregular sills, and were invaded also by certain masses of granite and quartz monzonite, including probably the Schultze granite, although this particular mass is not now in contact with the sedimentary series. All the rocks mentioned were covered wholly or in part by a thick flow of dacite, probably in early Tertiary time.

These rocks are cut by numerous faults, some older and some younger than the dacite.

The copper deposits occur (1) as lodes in schist, quartzite, limestone, and diabase, which, where they pass through or alongside of limestone, as in the Old Dominion mine, may be connected with large replacement bodies in that rock; (2) as disseminations of chalcocite ore in the Pinal schist near the Schultze granite (Miami and Inspiration mines); (3) as secondary deposits of chrysocolla in dacite tuff (Black Warrior mine) or in fissures (old Live Oak and Keystone workings).

The primary ore of the lodes consists essentially of pyrite and chalcopyrite, with bornite and specularite[1] of less regular or less abundant occurrence and galena and sphalerite rather rare. In the disseminated deposits in schist the primary metallic minerals are pyrite and chalcopyrite with a little molybdenite.

The disseminated primary metallization was undoubtedly connected with the intrusion of the Schultze granite, the constituents of

[1] This mineral had been seen at Globe only in association with oxidized ores when Professional Paper 12 was written.—F. L. R.

the sulphides probably emanating from the magma reservoir that supplied that rock. The lode ores were also deposited at high temperature and may also be genetically connected with the granitic magma. They are, however, more closely associated with the diabase, and possibly this rock had some share in their genesis. The known ore bodies in limestone have been modified by secondary processes, but their original deposition by replacement was apparently not associated with any important metamorphism of the adjacent limestone.[1]

The altitude of the Globe quadrangle ranges from 3,000 to 7,850 feet and the average annual precipitation is between 13 and 20 inches. The ground-water level is in general deep, although in parts of the areas occupied by the early Quaternary Gila conglomerate water is abundant within moderate distances from the surface. In the Old Dominion mine the original water level was probably between 700 and 800 feet in depth, and a large part of the present influx is derived from workings that tap the conglomerate-filled valley of Pinal Creek. In the Miami-Inspiration group of mines the underground water level is not very well defined. Generally some water appears below a depth of 400 feet, but as a rule water is not abundant at depths less than 900 feet.

The ore bodies in limestone of the Old Dominion and neighboring mines have been nearly exhausted. They were large irregular masses of oxide and carbonate ore associated with much limonite and hematite. In the lodes connected with these masses oxidized ore prevails generally to a depth of 700 to 800 feet but extends much deeper, as was predicted in 1903,[2] in the much-faulted ground under the Gila conglomerate, in the western part of the mine, where it is found on the 1,600-foot or bottom level about 1,200 feet below the surface. It is thus highly probable that much of the oxidation and enrichment at the Old Dominion lode was effected before the deposition of the Gila conglomerate.

Under the oxidized ore in the Old Dominion and adjacent lodes, mainly in diabase, are large bodies of chalcocitically enriched ore which grade irregularly downward into pyrite or into pyritic ore containing chalcopyrite, bornite, and specularite. In places enrichment has not penetrated below 800 feet, but elsewhere it goes much deeper.

The disseminated deposits near Miami, about 6 miles west of Globe, have been proved during the last few years to be of great economic importance. Churn drilling and mining exploration have shown the existence of a chain of large ore bodies extending in a gentle

[1] L. C. Graton (U. S. Geol. Survey Mineral Resources, 1907, pt. 1, p. 596, 1908) has stated that the ores in limestone are believed to be of contact-metamorphic origin. I am not in accord with this statement.—F. L. R.

[2] Ransome, F. L., Geology of the Globe copper district, Arizona: U. S. Geol. Survey Prof. Paper 12, p. 148, 1903.

curve from the Miami mine on the east through the Inspiration, Keystone, and Live Oak mines to the west. The extreme western limit of this ore belt is as yet undetermined. The total length of this chain as at present developed is 2 miles, the maximum width is one-fourth mile, and the greatest thickness of ore along any one vertical line is about 300 feet. Estimates by the engineers of the various mines give a total of 80,000,000 to 90,000,000 tons of ore averaging between 2 and 2.5 per cent of copper.

As a whole, the ore bodies form an irregularly undulating ribbon of very uneven thickness. The distance from the surface of the ground to the top of the ore differs widely from place to place and is not definitely related to the present topography, which apparently is of later development than the main period of enrichment. At the Miami mine the depth to ore is in general between 200 and 400 feet, on the Inspiration ground it ranges from 50 to 600 feet, and on the Live Oak ground it reaches 1,000 feet. The ore dips generally east in the Miami mine, is on the whole nearly horizontal in the Inspiration mine, but turns down to the west in the Keystone, and this westerly dip increases to 40° or 45° in the Live Oak ground. East of the Keystone a zone of strong faulting has stepped down the ore, and at the Miami mine another fault cuts off the ore by bringing the Gila conglomerate down against the schist. There are other important faults in the district, but these can not be described in this brief note.

The surface of demarcation between the leached, more or less rusty, barren schist and the top of the ore is definite, and in many places there has been some slipping between the capping and the ore. The downward change from ore (above 1.3 per cent copper) to primary material (less than 1 per cent copper) is less definite but takes place within a few feet.

The country rock is in general Pinal schist, but good ore occurs also in dikes and small offshoots that extend into metallized schist from the main granite mass, which grades into granite porphyry on its margins. Over much of the ore-bearing ground this granite porphyry is the surface rock, the ore occurring in the schist beneath it. Clearly this part of the porphyry was intruded as a flat-lying sheet.

In general the unmetallized Pinal schist is a bright-gray fissile rock, splitting with a lustrous satiny sheen and showing considerable variations in color, texture, and degree of metamorphism or crystallinity. The essential constituents are quartz, muscovite (sericite), a little microcline and plagioclase, magnetite, zircon, tourmaline, hornblende, biotite, and chlorite. As a whole, the Pinal schist was derived by metamorphism from arkosic sedimentary beds, although it includes here and there a little material of probable igneous origin.

During the primary period of metallization pyrite, chalcopyrite, a little molybdenite, and quartz were deposited in the fractured schists, partly in fissures an inch or so wide but chiefly in much smaller cracks or along cleavage planes. During the period of enrichment the downward-moving cupriferous solutions replaced the chalcopyrite and pyrite wholly or in part by chalcocite.

Final expression of opinion as to the geologic date of the principal enrichment is withheld, but a preliminary review of the evidence strongly suggests that the enrichment antedated the deposition of the Gila conglomerate and may possibly be older than the dacite. Probably the process has continued to the present day, but where erosion has overtaken the chalcocite zone enrichment apparently has been temporarily checked by the fact that little pyrite is available to form strongly acid solutions, and the copper, instead of migrating downward, remains near the surface, coloring the rocks brilliantly with chrysocolla and carbonates. As a rule, the largest ore bodies are not found under those surface rocks that are most vividly colored by copper compounds or by iron oxide.

RAY, ARIZONA.

By F. L. Ransome.

The disseminated copper deposits of Ray are about 20 miles southwest of Globe, in the hilly depression drained by Mineral Creek, between the Dripping Spring and Tortilla ranges.

The geologic formations are in general the same as those in the Globe quadrangle, the Pinal schist at Ray being intruded by two varieties of granite porphyry, one of which very closely resembles the porphyritic facies of the Schultze granite.

The ore bodies are mainly in the schist, although masses of granite porphyry within the generally metallized area have also been converted to ore.

Within the productive area the altitude ranges from 1,950 to 2,900 feet above sea, and most of the hills are steep and rugged. The climatic conditions are similar to those at Globe. Little information is available concerning the level of ground water, which is below the principal mine workings. Most of the water that enters the mines appears to be seepage from Mineral Creek and from its tributary, Copper Creek.

The ore bodies underlie a group of more or less rusty hills stained here and there with salts of copper. The principal area showing this alteration is of elongated oval shape and extends west-northwestward from Mineral Creek for about 2¼ miles with a maximum width of a little more than half a mile. Within this area churn drilling and mining have shown the presence of a continuous ore body about 8,000 feet long and 2,500 feet in greatest width. As at Miami, the layer of

ore has many irregular undulations that apparently have no dependence on the present topography and varies much in thickness. The average thickness of the ore body is 101 feet; the average thickness of overburden, 250 feet. The depth to ore ranges from 10 to 300 feet, and the thickness of the ore from 0 to 400 feet. Chalcocite has been reported from one drill hole to a depth of 715 feet, and the ore extends under Humboldt Hill to a depth of 700 feet. The quantity of ore in the Ray ore body as calculated by the mine engineers is over 83,000,000 tons averaging 2.17 per cent of copper, with over 500,000 tons of considerably higher grade.

The relations of the ore to the oxidized leached capping and to the underlying primary material are similar to those at Miami. The ore constituents in the two districts are the same. In both districts the primary metallization continues to unknown depths. As at Miami, the greater part of the chalcocite is disseminated through the schist (or porphyry) in small specks or in minute veinlets with quartz; but here and there are veinlets several inches wide in which the original chalcopyrite and pyrite have been partly or wholly altered to massive chalcocite.

Pyrrhotite, sphalerite, and galena, so far as known, do not occur in the disseminated copper deposits at Ray or Miami.

MORENCI, ARIZONA.

The Morenci district, Arizona,[1] is an area of pre-Cambrian granite and quartzitic schists above which rest unconformably about 1,500 feet of Paleozoic sandstones, limestones, and shales that are locally overlain by Cretaceous shales and sandstone. These rocks are intruded by masses of granitic and dioritic porphyries, which form stocks, dikes, laccoliths, and sheets. All these rocks have participated in an uplift and a warping or doming that was succeeded by much faulting, which took place during latest Cretaceous or earliest Tertiary time. Surrounding the domed area of older rocks are great masses of Tertiary lavas consisting of basalt and rhyolite, with some andesite.[2]

The ore bodies are veins and disseminated deposits in the granite and monzonite porphyry and contact-metamorphic deposits in the limestone and shale near the porphyry. The fissure veins and nearly related disseminated deposits are most productive. In 1906, according to Graton, over 92 per cent of the production came from the large disseminated deposits and stockworks of chalcocite along shattered zones in altered porphyry.[3]

[1] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, 1905.

[2] Idem, p. 17.

[3] Graton, L. C., U. S. Geol. Survey Mineral Resources, 1906, p. 388, 1907.

Lindgren[1] summarizes the successive stages of mineral formation as follows:

Veins:

Primary processes: Pyrite, chalcopyrite, zinc blende, molybdenite (rarely magnetite), sericite, quartz (rarely tremolite, diopside, and epidote). Introduction of iron, sulphur, zinc, copper, potassium, and silica; elimination of calcium and sodium.

Processes of oxidation:

Action of sulphate solutions without oxygen: Chalcocite (rarely covellite, chalcopyrite, and bornite), quartz, chalcedony, kaolin, alunite. Introduction of copper; elimination of zinc, some iron and sulphur.

Action of directly oxidizing solutions: Cuprite, native copper, brochantite, malachite, chrysocolla (rarely azurite), chalcanthite, limonite, quartz. Introduction of carbon dioxide; elimination of sulphur, together with some iron and copper.

Contact deposits:

Primary processes: Pyrite, magnetite, chalcopyrite, zinc blende, garnet, epidote, diopside, tremolite, quartz. Introduction of much iron and silica, together with copper, zinc, molybdenum, sulphur, possibly magnesia; elimination of carbon dioxide and probably some lime.

Processes of oxidation: Limonite, malachite, azurite, cuprite, rarely native copper and chalcocite, copper-pitch ore, chrysocolla, goslarite, zinc carbonate, willemite, calamine, pyrolusite, quartz, calcite, chlorite, serpentine. Introduction of carbon dioxide and additional copper; elimination of calcium, sulphur, some zinc, and iron.

The veins rarely show typical gossan or iron cap with an abundance of limonite and rich oxidized ores. Their outcrops are either entirely barren or contain only a moderate amount of copper, but much richer ore is ordinarily found just above the chalcocite zone. The upper half of the chalcocite ore is richer. It occurs as solid masses and in the porphyry as scattered grains. In both classes of deposits it replaces pyrite and zinc blende, and generally at a depth rarely more than 400 feet below the surface it gives way to these minerals, which form a very low-grade unworkable ore. The annual rainfall is about 10 inches. No standing ground-water level has yet been encountered, and the upper parts of the chalcocite bodies are undergoing extensive oxidation.

The deposits in porphyry, as stated by Lindgren, generally show the following arrangements in depth:[2]

Surface zone.....50 to 200 feet deep from the croppings; contains oxidized copper minerals or is barren.

Chalcocite zone....100 to 400 feet in vertical extent; possibly more in places; contains chalcocite and pyrite.

Pyritic zone.....Begins 200 to 600 feet below the surface; contains pyrite, chalcopyrite, zinc blende, and molybdenite.

The minerals of the upper two zones have been derived from those of the pyritic zone by processes of direct and indirect oxidation; the

[1] Lindgren, Waldemar, op. cit., p. 194. [2] Idem, p. 201.

chalcocite is derived from replacement of pyrite and sphalerite probably by aid of cupric sulphate solutions. The surface zone has been derived from the chalcocite zone by its gradual and direct oxidation. The pyritic zone has thus far been found to be poor in copper and rarely makes commercial copper ore; the chalcocite zone produces the richest ore and the richest part of it is near its upper limit; the leached zone is usually poor and in some places practically barren. These changes with depth may be observed also in the contact-metamorphic ores, but these ores as a rule are not altered to depths so great.

The Coronado vein, which occupies a fault fissure between pre-Cambrian granite and quartzite, differs in many respects from the deposits in the porphyry, and it is suggested by Lindgren[1] that it probably had a different origin. The ore minerals include pyrite, chalcopyrite, and chalcocite. Sphalerite is not mentioned by Wendt[2] or by Lindgren as a vein constituent, although it appears in appreciable quantities in other ores in this district. Lindgren notes that chalcocite ore is found in this vein as deep as 500 or 600 feet below the surface. More recently, according to Tolman,[3] a chalcocite zone has been found in the Coronado mine considerably deeper than in any other mine in the district.

ELY, NEVADA.

By A. C. Spencer.

The Ely district, Nevada,[4] is an area of folded and faulted Paleozoic limestones and shales ranging in age from Ordovician to Carboniferous. These formations are intruded by monzonite porphyry along an east-west zone about 9 miles long and from one-half to 1 mile wide. These older formations are locally overlain by rhyolite flows of Tertiary age. The sedimentary rocks adjacent to the porphyry intrusions are greatly altered, being locally garnetized or changed to jasperoid and commonly charged with great quantities of pyrite. In places near the igneous masses considerable amounts of chalcopyrite occur with the pyrite, and rarely zinc blende and pyrrhotite accompany these sulphides. Galena and its oxidation products occur in irregular lodes within the metamorphic area, principally at some distance from the porphyry masses. Gold ores formerly exploited occur mainly in the form of blanket lodes, the gold being associated with lead carbonate.

[1] Lindgren, Waldemar, op. cit., p. 344.

[2] Wendt, A. F., The copper ores of the Southwest: Am. Inst. Min. Eng. Trans., vol. 15, pp. 28–52, 1887.

[3] Tolman, C. F., The southern Arizona copper fields: Min. and Sci. Press, vol. 99, p. 390, 1909.

[4] Lawson, A. C., The copper deposits of the Robinson mining district, Nevada: California Univ. Dept. Geology Bull., vol. 4, pp. 287–357, 1906. Spencer, A. C., Preliminary geologic map of the vicinity of Ely, Nev., U. S. Geol. Survey, 1912.

Of many superficial showings of copper carbonates none has been developed profitably, but oxidized ores of relatively high grade have been discovered in the Alpha mine of the Giroux Co. at considerable depth. This ore body is inclosed by metamorphosed and thoroughly oxidized sedimentary rocks that lie several hundred feet from the nearest mass of porphyry.

The present importance of the district centers in the low-grade disseminated ores in porphyry. The igneous rock was locally fractured after its intrusion, and great masses of it became infilled with veinlets of quartz carrying pyrite and chalcopyrite. Even away from the fractures the porphyry was charged with sulphides and the rock was greatly altered, lime, magnesia, soda, and iron being abstracted and a noteworthy amount of potash added. These losses and gains involved the destruction of hornblende and lime-soda feldspar and the formation of mica, including brown mica and sericite. The outcrops of the ore masses are yellowish or less commonly red and are said to carry not over 0.5 per cent of copper. There is an abrupt change from this capping to soft bluish-white porphyry ore, which carries disseminated sulphide minerals, including copper glance, as films coating grains of pyrite and chalcopyrite or, less commonly, completely replacing such grains.

One company—the Nevada Consolidated—has developed about 49,000,000 tons of disseminated ore, the average being 1.7 per cent copper. The variations in depth are indicated in three sections, as follows:[1]

Thickness, in feet, of capping and of ore in workings of the Nevada Consolidated Co., Ely, Nev.

Section.	Average thickness of direct capping.	Average thickness of profitable ore.
	Feet.	*Feet.*
Eureka	87.1	190
Hecla	101.4	280.3
Liberty	154.7	193.3
Average	102.5	217.9

The profitable ore is known to extend locally to depths about 600 feet below the surface. In one place a hole was put down nearly 400 feet below the ore body in material which carried less than 0.4 per cent of copper.

The gold and silver content of the disseminated ores is considerable. In 1911 the average per ton was 0.013 ounce gold and 0.079 ounce silver. Although less than 60 per cent of the precious metals was saved, their value recovered was 17.35 cents a ton.

[1] Nevada Consolidated Copper Co. Fifth Ann. Rept., for 15 months ended Dec. 31, 1911, p. 8.

A composite analysis of 1,000 samples of ore from the Ruth mine shows, as stated by Lawson, sulphur, 6 per cent; iron, 5.3 per cent; and copper, 2.61 per cent, which may be calculated as approximately equivalent to pyrite, 10 per cent; chalcopyrite, 1.8 per cent; and chalcocite, 2 per cent.

It may be stated as a general truth that any porphyry carrying more than 1 per cent of copper owes its grade to the presence of chalcocite, the enrichment having resulted from precipitation of this mineral out of solutions derived from overlying material.

In the porphyry mines the lower limit of complete oxidation is everywhere considerably above the water level, the difference in elevation being about 250 feet in the Ruth mine. Though most of the material carrying chalcocite lies above standing water, the bottom of the ore seems to bear no definite relation to the water table. The greatest depth of porphyry ore is about 600 feet, but in the Alpha mine, which lies outside of the porphyry ore, enriched ore was found between the 700 and 1,200 foot levels. Here the water stands somewhat more than 1,000 feet below the surface and most of the lode material is fully oxidized and leached to that depth.

SANTA RITA, NEW MEXICO.

The Santa Rita district[1] is in the Silver City quadrangle in southwestern New Mexico. The recent developments there of the Chino mine have shown that it is one of the most important copper districts in the United States. The country comprises an area of Silurian, Devonian, and Carboniferous quartzites and limestones, and above these unconformably lie Cretaceous quartzites and schists. Above the Cretaceous rocks, also unconformably, lie Tertiary lavas and tuffs. The Cretaceous and older rocks, as stated by Paige, are intruded by diorite and associated igneous rocks, by quartz diorite porphyry, and by quartz monzonite and quartz monzonite porphyry, chiefly as laccoliths. Subsequently, in Tertiary time, the rhyolite flows and intrusions and basalt flows were formed. Folding attended the intrusions of diorite and faulting followed the extravasation of Tertiary lavas. Finally Quaternary sediments with interbedded basalts were deposited. Zones of garnet are extensively developed in limestone and, according to Paige, the quartz monzonite porphyry has greatly metamorphosed the quartz diorite porphyry intrusives by the development of sericite, epidote, and quartz, and the recrystallization of the iron in the dark silicates to form sul-

[1] Paige, Sidney, The geologic and structural relations at Santa Rita (Chino), N. Mex.: Econ. Geology, vol. 7, pp. 547–559, 1912; U. S. Geol. Survey Geol. Atlas, Silver City folio (No. 199), 1916. Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 305, 1910.

phides. The quartz monzonite porphyry carries most of the disseminated ore. It is highly sericitized and carries sulphides and secondary silica. By oxidation iron oxides and kaolin have been formed. The primary mineralization followed the deposition of the Cretaceous quartzite and preceded the extravasation of the Tertiary lavas. According to Paige the country was peneplained after the ore was deposited, before Tertiary time, and probably enrichment was then well advanced.

At Santa Rita most of the copper occurs as native metal, oxide, or sulphide in altered porphyry. Chalcocite with kernels of pyrite is disseminated both in the quartzite and in the porphyry,[1] and much of the chalcocite has doubtless replaced pyrite. Outside the bodies of copper ore pyrite is distributed similarly to the chalcocite within the ore bodies.

As stated by Graton, some of the copper that now exists as native metal or oxide was not precipitated on pyrite but was deposited as sulphide in open spaces and in porphyry as replacement along fissures.

In the disseminated ores on the Chino ground some 90,000,000 tons of ore averaging 1.75 per cent copper are said to be developed. Most of it is near the surface. It is said that nearly all of it may be mined with steam shovels. The average thickness of the capping, according to B. S. Butler,[2] is 82 feet, and the average thickness of the ore below the capping is 107 feet.

The ore is somewhat richer than the disseminated ore in several other districts in the Southwest, but no data are available to show that zinc blende has favorably affected the grade of the concentration. I am informed that sphalerite is present in some of the deposits, but that little or none has been observed in the ore directly below some of the important bodies of disseminated ore.

BURRO MOUNTAIN DISTRICT, NEW MEXICO.

The Burro Mountain district[3] is in Grant County, N. Mex. The country is arid and stands 5,000 to 8,000 feet above sea level. The main mass of the mountains consists of pre-Cambrian granite and pegmatite and dioritic rock, which is locally gneissic. These rocks are intruded by quartz porphyry and by quartz monzonite porphyry. Remnants of volcanic breccia, probably Tertiary, cap the older intrusive rocks.

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[1] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., op. cit., p. 62.

[2] Butler, B. S., U. S. Geol. Survey Mineral Resources, 1910, pt. 1, p. 205, 1911.

[3] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 322–323, 1910. Lang, S. S., The Burro Mountain copper district: Eng. and Min. Jour., vol. 82, p. 395, 1906. Paige, Sidney, Metalliferous ore deposits near the Burro Mountains, Grant County, N. Mex.: U. S. Geol. Survey Bull. 470, p. 131, 1910. Somers, R. E., The Burro Mountain copper district: Am. Inst. Min. Eng. Bull. 101, pp. 957–996, 1915.

The monzonite porphyry and quartz porphyry are locally fractured and are traversed by innumerable small joints and fissures. The fracture zone in the principal mineralized area is believed by Somers to have been formed by stresses that attended the extrusion of lavas; that it is not caused by contraction of the monzonite on cooling is evident, for only a small part of the monzonite mass is fractured.[1] In these fractures and in the wall rock between them much quartz, pyrite, chalcopyrite, and sphalerite have been deposited. Sericite and quartz have been developed in the wall rock by hydrothermal metamorphism, particularly near the veins. The ore near the surface is leached of the sulphides; limonite, hematite, chalcedony, and kaolin mark the outcrops. With these minerals in the oxidized zone are associated some malachite, azurite, and chrysocolla and small quantities of cuprite and native copper. Below the surface a zone of chalcocite having a maximum thickness of 200 to 300 feet is developed over most of the mineralized area. The rock in this zone carries about 2 or 3 per cent copper. In it chalcocite has replaced pyrite, chalcopyrite, and sphalerite. Bornite and covellite ore was not observed.[2] Below the chalcocite zone is low-grade material, carrying pyrite and finely divided chalcopyrite and sphalerite.

The country slopes gently from the summit of the Big Burro Mountains to the Mangas Valley. The two principal camps are Tyrone, near the valley, and Leopold, higher on the slope. At Tyrone, where erosion has been slow, the leached zone locally extends several hundred feet below the surface and the chalcocite zone lies at considerable depths. At Leopold, where erosion has probably been more rapid, because the country was higher, the chalcocite zone is at some places within 50 feet of the surface or less. At depths of 200 to 300 feet below the surface the primary material or protore is found.

The zone of enrichment does not show a close relation to the present water level, which lies at depths of 275 feet to 400 feet. At Tyrone chalcocite ore is found both above and below the water level; at Leopold considerable masses are found above the water level. Somers believes that the ore was not precipitated to any great extent above the water level because the ground is fractured and open but that its occurrence in part above the present water level is due to the fact that the water level migrates downward more rapidly than the ore. At Leopold, where erosion has been more rapid, the water level has moved downward more rapidly, and the chalcocite zone, which has moved but slowly, is therefore more generally above the water level than at Tyrone. It is nearer the surface also because erosion has removed the leached zone at a more rapid rate at Leopold than at Tyrone.

[1] Somers, R. E., op. cit., p. 979. [2] Idem, p. 984.

CANANEA, MEXICO.

Cananea, Sonora, Mexico, is 25 miles south of the international boundary and about 38 miles by rail from Bisbee, Ariz. The country is mountainous, and the principal deposits are 5,200 to 6,500 feet above the sea. The climate, although arid, is somewhat more humid than that of Arizona.

The region has had a complex geologic history.[1] An ancient granite is overlain by Paleozoic (?) quartzite and limestone and intruded by diabase, above which are rhyolitic tuffs and rhyolite. Intrusive masses of syenite and syenite porphyry are later than the sedimentary rocks and probably later than the tuffs, and large intrusive masses of diorite and diorite porphyry cut both tuffs and limestones. A later granite porphyry, a granodiorite, a quartz monzonite porphyry, gabbro, and diabase are found in intrusive masses.[2]

Contact metamorphism, with the development of heavy silicates and sulphides, has attended the intrusion of the diorite porphyry, the granodiorite, and the quartz porphyry. Contact-metamorphic deposits are numerous and important, but these are subordinate to the great lodes and disseminated ores in the sericitized and silicified phases of the diorite porphyry. The principal deposits of the latter class lie in a belt 1 to 2 miles wide and 6 miles long, which strikes a little north of west, significantly parallel to the great Eliza fault. The contact-metamorphic deposits are composed of chalcopyrite, sphalerite, bornite, magnetite, hematite, and galena in a gangue of garnet, calcite, hornblende, pyroxene, and other heavy silicates. In general, these deposits show chalcocite enrichment to only very shallow depths.[3]

The ores in porphyry are composed chiefly of pyrite, chalcopyrite, sericite, kaolin, quartz, and other minerals. Zinc blende, although locally abundant, is erratic in distribution. In these ores chalcocite enrichment is very extensive.

Many of the ore bodies are marked by conspicuous gossan immediately or not far above the deposits. This, I believe, is invariably true of the garnetiferous ores in altered limestone, although in these ores oxidation extends only to shallow depths. Some richer ores of this type are seamed and coated with chalcocite, and possibly some chalcopyrite in these deposits is secondary, but these ores are never-

[1] Emmons, S. F., Cananea mining district of Sonora, Mexico: Econ. Geology, vol. 5, pp. 312–356, 1910.

[2] Weed, W. H., The Cananea copper deposits: Eng. and Min. Jour., vol. 74, pp. 744–745, 1902; The Cananea district: Am. Inst. Min. Eng. Trans., vol. 32, p. 428, 1902; The Cananea ore deposits: Eng. and Min. Jour., vol. 76, p. 383, 1903. Austin, W. L., The ore deposits of Cananea: Eng. and Min. Jour., vol. 76, pp. 310–311, 1903. Hill, R. T., The ore deposits of Cananea: Idem, p. 421; Cananea revisited: Idem, pp. 1000–1001. Elsing, M. J., Relation of outcrops to ore at Cananea: Eng. and Min. Jour., vol. 95, pp. 357–359, 1913.

[3] Emmons, S. F., op. cit., p. 355.

theless workable at several places, in what to me appears to be their primary concentration.

In the West Cobre Grande and Kirk mines the development is in both diorite porphyry and limestone. The ores are generally of good grade, but at the 200-foot level there is an apparent falling off in the amount of chalcocite and an increase in the proportion of zinc in the ore, which indicates sulphide enrichment.[1]

The most important deposits of the district are those of the Capote basin, which are largely fractured zones in sericitized porphyry. The primary ores consist mainly of pyrite with a small admixture of chalcopyrite and in places considerable zinc blende. Their introduction was accompanied by extensive sericitization and silicification of the adjoining country rocks. They occur in closely spaced fractures or shear zones that traverse both eruptive and sedimentary rocks and adjoining fractures, and they are disseminated in porphyry throughout the rock. The tenor in copper is so low that it is doubtful if the primary ore could have been mined at a profit if it had not received additional copper by downward migration or sulphide enrichment.[2]

The surface is conspicuously altered by oxidation, which has readily attacked the hydrothermally altered pyritized area. Along the Capote fault zone the ore body is capped by gossan, which lies above porphyry and quartzite. A chimney of ore, large on level 1, was followed down to level 7, where it had decreased in size. This chimney of ore appears to represent a zone of intense fracturing and one peculiarly favorable to concentration. Some of the fracturing is later than primary deposition, for traces of enrichment are found down to the seventh level.[3]

The Oversight ore body is capped by porphyry that is silicified but only slightly stained with iron. The chalcocite ore is found 260 feet below the surface and extends downward at least 300 feet deeper, but its lower limit had not been determined in 1907.

The Veta Grande ore body has produced remarkably rich oxidized ore, chiefly cuprite and native copper. Rich ore of decreasing tenor was found as deep as the 500-foot level. In the middle levels there is much enrichment by chalcocite, but this enrichment has apparently not extended to the lowest level.[4]

NACOZARI, MEXICO.

Nacozari, Sonora, Mexico, is 75 miles south of the international boundary line, in a region of hills and low mountain ranges much like those of Arizona. The country rock consists of volcanic tuffs,

[1] Emmons, S. F., op. cit., p. 340.
[2] Idem, p. 341.
[3] Idem, p. 345.
[4] Idem, p. 347.

breccias, and other igneous rocks, with which are associated subordinate limestones and other sedimentary rocks.[1]

The most important mines belong to the Moctezuma Copper Co., controlled by Phelps, Dodge & Co. The principal developments are those of Los Pilares mine, at the end of a tunnel about a mile long, which intersects a shaft 600 feet below the surface. The largest deposit is a great semicircular body of relatively low grade ore that appears to conform with a curving fractured mass of monzonite (?) which follows a sheeted zone of faulting and a faulted diabase dike that intersect nearly at a right angle.

The ore in depth is composed of brecciated monzonite (?) the small fragments of which are cemented by iron and copper sulphides. The principal sulphides are pyrite and chalcopyrite, which in the richer ore are coated with bornite and a relatively small amount of chalcocite. In places the ore contains a little zinc, but lead is not reported to be present. At the surface the outcrop is iron-stained gossan that has locally weathered into the pillars from which the mine derives its name. As in some other arid regions, the iron ore has become dehydrated at the surface, forming specularite. The stopes of richer ore extend from a short distance below the 100-foot level down nearly to the 500-foot level. Below this the ore is said to be falling off in grade.

> It is thus evidently to secondary enrichment that it owes its quality as pay ore. Above these limits the copper is leached out; within them is the greatest concentration of the richer sulphides and, while they can still be observed in the lower levels of the mine, it is evident to the eye that they are in decreasing proportion.[2]

According to W. L. Tovote[3] the chalcocite zone is insignificant.

AJO, ARIZONA.

The Ajo district,[4] in south-central Arizona, contains disseminated copper ores in porphyry, in which oxidation appears to have been attended by little leaching and chalcocitization. The most notable geologic feature of this region is a great laccolith or batholith of monzonite porphyry, 8 or 10 miles long by 1 to 4 miles wide, which has domed up the older rhyolite beds.

Some rich copper veins occur in the porphyry and in the rhyolite, but the most valuable deposits developed are in a mass of shattered

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[1] Emmons, S. F., Los Pilares mine, Nacozari, Mexico: Econ. Geology, vol. 1, pp. 629–643, 1906.

[2] Idem, p. 636.

[3] Tovote, W. L., Magmatic origin of ore-forming solutions: Min. and Sci. Press, vol. 104, p. 602, 1912.

[4] Joralemon, I. B., The Ajo copper-mining district: Am. Inst. Min. Eng. Trans., vol. 49, p. 593, 1915.

porphyry that occupies about 55 acres and has a maximum depth of 600 feet, carrying about 12,000,000 tons of carbonate ore, below which lie about 28,000,000 tons of sulphide ore. Unlike the disseminated deposits at Bingham, Ely, and Santa Rita, in which the copper ore is largely chalcocite, the disseminated ores in the Ajo district are chalcopyrite and bornite. The porphyry is highly shattered. Along some of the larger fractures the seams of bornite and chalcopyrite widen to veins an inch or more across. Where several of these veins are parallel and closely spaced there are bands of ore, 10 to 100 feet wide, assaying from 3 to 5 per cent copper. The grade of the ore in general is extremely variable, changing abruptly from porphyry containing less than 0.5 per cent copper to ore assaying over 3 per cent.[1] There are excellent examples of replacement of bornite by chalcocite, but these are said to be quantitatively unimportant.[2]

The outcrop and oxidized zone is silicified monzonite porphyry, with seams and stains of malachite, limonite, hematite, and a little chrysocolla. The feldspars are partly kaolinized. About 85 per cent of the copper in the oxidized zone is said to be malachite. Here and there disseminated chalcopyrite and bornite remain unaltered in hard ore between fractures, but such remnants of sulphides are insignificant compared with the great mass of carbonate ore. The oxidized ore extends downward to an almost horizontal plane about 20 feet below the deepest arroyos and 150 feet below the highest hills. This plane is approximately the present ground-water level, and the transition from carbonate to sulphide ore is very abrupt. In general the drill cores show less than 5 feet of partly oxidized ore.[3] Oxidized and sulphide ore each average about 1.5 per cent copper.

East of the ore body, where the disseminated copper sulphides give place to pyrite, the oxidation extends to practically the same horizontal plane at water level. The ore of the oxidized zone, however, is not hard and siliceous but soft, and it contains much kaolin and limonite and little copper stain. Instead of standing up in bold brown and green cliffs, the outcrops are reddish and form valleys or low hills. The oxidized zone contains much more limonite and alumina, but less silica and very little copper. At the top of the lean pyritic material there is a 5-foot or 10-foot zone of enriched chalcocite ore carrying 1.5 to 3 per cent copper. The sequence in this part of the Ajo basin is closely similar to that in many other disseminated chalcocite deposits, but the primary mineralization was

[1] Joralemon, I. B., op. cit., p. 599.

[2] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper: Am. Inst. Min. Eng. Trans., vol. 45, p. 78, 1914.

[3] Joralemon, I. B., op. cit., p. 601.

too lean in copper or the leached zone was too shallow to form an enriched ore body of commercial value.

Joralemon considers the carbonate deposits oxidized primary ores. There has been some chalcocitization, but the downward transfer of copper appears to have been halted. The relations might be due to rapid erosion and to a downward migration of the water level that was rapid compared to the leaching, which in an arid country where the quantity of iron sulphide was not large was necessarily slow.

SILVERBELL, ARIZONA.

The Silverbell district[1] is in the western part of the Silverbell Mountains, about 40 miles west of Tucson. The area is rugged and the climate is dry and hot. The country consists of blocks of Paleozoic limestone completely surrounded by later intrusive rocks—alaskite, alaskite porphyry, biotite granite, andesite, and quartz porphyry—which, according to Stewart, were formed in the order stated. Contact garnet zones containing andradite, wollastonite, and quartz have been formed in the limestone, the garnetization accompanying both alaskite porphyry and biotite granite intrusives. The ore deposits are contact-metamorphic deposits of copper ores, disseminated copper ores in porphyry, and lead-silver fissure veins. Up to 1909, when the district had produced 11,000,000 pounds of copper, the contact-metamorphic deposits had supplied most of the ore. The unoxidized contact-metamorphic deposits carry pyrite and chalcopyrite in a gangue of garnet, wollastonite, quartz, and calcite; also a little bornite, probably secondary, and a little chalcocite. The garnet ores are heavy, black, and copper-stained on their outcrops, and are oxidized to a depth of about 250 feet, the depth depending on the extent of the fracturing. The ore in this zone is much enriched by the formation of copper oxides and by the leaching out of calcite and sulphur. In this zone hematite and a copper oxide, probably cuprite, are abundant, and carbonates, chrysocolla, wulfenite, barite, and molybdenite also occur. The ore carries not more than 1 ounce of silver to the ton. A sulphide deposit that contains 2 or 3 per cent of copper in the sulphide zone will contain 10 or 12 per cent in the oxidized zone. Very little copper has been leached out of the oxidized zone, probably because the gangue contains calcite, which tends to delay the solution of copper in sulphuric acid and to precipitate the minerals of the oxidized zone. It is noteworthy, however, that much oxide and very little malachite and azurite have formed.

[1] Stewart, C. A., The geology and ore deposits of the Silverbell mining district, Arizona: Am. Inst. Min. Eng. Trans., vol. 43, pp. 240–290, 1913. Tolman, C. J., jr., Copper deposits of southern Arizona: Min. and Sci. Press, vol. 99, pp. 710–712, 1909.

The unoxidized alaskite porphyry, alaskite, and granite are silicified, sericitized, and contain copper-bearing pyrite, and these rocks on weathering are locally somewhat stained with copper minerals. Churn drilling has revealed disseminated chalcocite ore at many places, but rarely enough to justify the extensive operations necessary to work the ore profitably. One hole, according to Stewart, shows 60 feet of 2 per cent ore. The chalcocite occurs as minute stringers and specks in alaskite. It usually has a core of unaltered pyrite and is associated with pyrite cubes coated with chalcocite and some pseudomorphs of chalcocite after pyrite. The oxidized zone extends generally to a depth not more than 100 feet, and the zone of secondary sulphides is 50 to 60 feet thick. Some holes have gone through a chalcocite zone into an oxidized zone and then back to chalcocite, and, as stated by Stewart, it is common to pass through bright, fresh pyrite before reaching the chalcocite.

The lead-silver ores are now commercially unimportant. One deposit described by Stewart[1] is a breccia vein filling a fault fissure in quartz porphyry. The ore is galena in a gangue of fluorite, calcite, quartz, and fragments of quartz porphyry. Considerable cerusite and anglesite occur in the upper part of the vein, which contains also, it is said, native silver and cerargyrite. In the garnet zone in an old lead-silver working near the Mammoth shaft, are great quantities of fluorite, which is not found in the contact ores proper. These ores Stewart considers to be later than the garnet ore.

SAN FRANCISCO REGION, UTAH.

By B. S. Butler.

The San Francisco region, Utah, is a large mineralized area in the San Francisco and adjacent ranges in Beaver County, Utah. The sedimentary series consists of Paleozoic limestones, shales, and quartzites. These have been covered by a thick series of lavas of intermediate composition. These formations have been intruded by quartz monzonite and allied rocks.

The ore deposits may be divided into three general types—(1) replacement deposits in fissures in the quartz monzonite; (2) replacement deposits in the limestone, including contact deposits and replacement deposits along fissures, and (3) replacement fissure deposits in the lavas.

Of the replacement deposits in fissures in the quartz monzonite the ore zone in the Cactus mine is the most important. This is a brecciated zone of quartz monzonite that has been greatly altered and replaced by the ore minerals. These are pyrite and chalcopyrite, small amounts of tetrahedrite and galena, and abundant specularite

[1] Stewart, C. A., op. cit., p. 502.

in a gangue of quartz, sericite, tourmaline, impure siderite, anhydrite, and some barite. Oxidation has not extended below 100 feet and for the most part is confined to a space within 50 feet of the surface. The principal minerals resulting from the oxidation are limonite, azurite, and malachite, with some native copper. Chalcocite is almost and possibly entirely absent from the deposit.

The O K mine, in the Beaver Lake Range, also works a deposit that lies in quartz monzonite and that is similar to the deposit worked by the Cactus mine except that it contains no specularite and that the gangue is quartz and sericite. In this deposit oxidation has extended to much greater depth, fully 200 feet, and covellite and chalcocite replace pyrite and chalcopyrite. The only apparent reason for the difference in the secondary ores here and in the Cactus mine is the presence in the latter of carbonate, which has probably prevented or retarded the downward movement of the copper content of the ores.

The typical contact deposits are composed of pyrite, chalcopyrite, magnetite, and sphalerite in a gangue of garnet, tremolite, and other silicates. In general oxidation has not extended to great depth, probably owing to the massive character of the deposits. The richer ores, however, have resulted from concentration in the oxidized zone.

The replacements along fissures in the limestone are typically lead-silver deposits containing minor amounts of copper and zinc. The ores are largely oxidized to the depth of present developments—500 to 600 feet. The metal-bearing minerals are principally carbonates but include minor amounts of sulphates.

The Horn Silver mine is on the most important deposit in the volcanic rocks. This deposit occurs along a fault that has thrown the lavas down against the Paleozoic limestone. The lavas have been considerably shattered along this fault, especially in the vicinity of minor cross faulting, but the limestone is relatively massive. The ore deposits have formed largely as replacements of the brecciated lavas. The primary ore consists of pyrite, galena, sphalerite, and minor amounts of other metallic minerals in a gangue of quartz, sericite, and partly altered lava. In the oxidized zone the ores are characteristically sulphates, anglesite being the principal mineral in much of the lead ore. Complex sulphates, such as beaverite, plumbojarosite, and jarosite, are rather abundant, and the oxidized copper ore carries much brochantite. Zinc is not abundant in the oxidized ores, though some carbonate of zinc occurs. In the secondary sulphide zone the copper ore consists of covellite and chalcocite, partly or wholly replacing sphalerite, wurtzite, pyrite, and, to a slight extent, galena. Rich copper ores were mined to a depth of about 750 feet, and enrichment along favorable channels has extended much deeper. The rich zinc ores of this mine are composed of sphalerite,

and wurtzite, together with the sulphides of other metals in variable quantities. The wurtzite is apparently secondary, commonly forming around cores of sphalerite, and the richer ores have resulted from the addition of the zinc in the wurtzite. Normally the zinc enrichment extends to greater depth than the copper enrichment, and secondary zinc sulphide has been replaced by secondary copper sulphides.

The Beaver Carbonate mine, another replacement deposit in the volcanic rocks, is similar in occurrence to the Horn Silver deposit, except that both walls are of the volcanic rock. In this deposit enrichment has been slight, apparently owing to the presence of a local water table very near the surface.

YERINGTON, NEVADA.

The country at Yerington, Nev., is an area of schists and limestone with intrusive masses of granodiorite, or quartz monzonite, and related porphyries, which are overlain by a series of rhyolite flows and tuffs, bedded volcanic grits, andesite tuff, and andesite breccia, and an unconformably overlying flow of basalt.[1]

The copper deposits, according to Ransome, are (1) irregular bodies formed by metasomatic replacement of limestone and genetically associated with metamorphism of a kind usually attributed to the contact action of intrusive rock, (2) metasomatic vein deposits in altered limestone, and (3) metasomatic vein deposits in granodiorite.

To the first or contact-metamorphic class belong the deposits worked by the Bluestone, Mason Valley, and other mines. In the Bluestone mine the ore consists essentially of chalcopyrite disseminated as grains and small irregular masses through limestone that has been altered to an aggregate consisting chiefly of a yellowish-gray epidote with subordinate calcite and quartz. A little garnet is present.[2] Zinc blende is not mentioned. In these deposits, as stated by Ransome,

> Oxidation is not extensive and scarcely penetrates to the 100-foot level, while chalcopyrite is present in the croppings. The products of oxidation are malachite (with possibly some brochantite and libethenite), azurite, cuprite, and chalcanthite. These are generally associated with sulphides, and there are no large masses of thoroughly oxidized ore. A little chalcocite occurs above the 100-foot level, but there has been no important enrichment through the secondary formation of this mineral. It is evident that the ore body as a whole is too solid to have been penetrable to any considerable depth by oxidizing solutions and that erosion has kept pace with the process of weathering.[3]

[1] Ransome, F. L., The Yerington copper district, Nevada: U. S. Geol. Survey Bull. 380, p. 99, 1909.
[2] Idem, p. 107.
[3] Idem, p. 108.

The vein deposits in limestone are represented by the Ludwig vein, which is composed mainly of coarse crystalline calcite carrying some garnet with pyrite and chalcopyrite. Oxidation in this deposit has extended to a depth of about 500 feet and has produced ore of shipping grade. At the base of the oxidized zone there has been some chalcocite enrichment.[1]

The primary ore of the Mason Valley mine contains more pyrite with the chalcopyrite than that of the Bluestone mine and appears to be generally of lower grade. Oxidation, however, has penetrated deeper and has effected some local concentration down to the No. 3 tunnel, although some sulphides occur at the surface. On the No. 3 level there is a considerable body of rich ore consisting of impure earthy cuprite with much disseminated native copper. The shape and extent of this body, which contains up to 20 per cent of copper, have not been fully ascertained. Chalcocite in a soft, sooty condition occurs sparingly, but there has been no important enrichment through the formation of this sulphide. The minerals noted in the oxidized zone are malachite, azurite, cuprite, native copper, limonite, gypsum, and chalcanthite.[2]

JEROME, ARIZONA.

By F. L. Ransome.[3]

At Jerome faulting has effected the relative elevation and exposure of a mass of pre-Cambrian schist, within which the principal ore bodies thus far developed are those of the United Verde mine. On the hillside just west of the mine the schist is unconformably overlain by Cambrian, Devonian, and Carboniferous beds.

In the vicinity of the mine the schist stands nearly vertical, with rather rough, irregular cleavage, and strikes a little west of north. At least three varieties are distinguishable—(1) a green rock, schistose on its margins but grading into massive material, which is evidently an altered dioritic intrusive; (2) a rough gray schist with abundant phenocrysts of quartz, apparently an altered rhyolite; and (3) satiny greenish-gray, very fissile sericitic schist that may be a metamorphosed sediment. The ore occurs in varieties 2 and 3, the main belt of dioritic rock (1) lying just west of the ore bodies. The ore is said to follow as a rule the layers of fine sericitic schist.

The ore shoot as a whole is of oval plan, its total horizontal length being about 1,300 feet and its greatest width 700 feet. Its general trend is north-northwest and it pitches in that direction at an angle of 45°. It has been worked to a vertical depth of 1,200 feet with no sign of approaching exhaustion. This great shoot is in reality a complex of smaller but nevertheless large irregular or lenticular ore bodies, apparently related in part to cross-fissuring but showing a general tendency toward parallelism with the schistosity.

[1] Ransome, F. L., op. cit., p. 117. [2] Idem, p. 110. [3] Based on a brief visit in 1912.

The important ore constituent is chalcopyrite, associated with varying proportions of pyrite and sphalerite. Bornite has been reported but was not noted in 1912. Neither galena nor pyrrhotite was observed at the time of visit. The sulphides occur partly in small irregular fractures and along planes of schistosity, but to a large extent they have metasomatically replaced the schist, particularly the fine-grained sericitic variety. The ore contains very little vein quartz or other gangue mineral.

The sulphides mentioned are primary and were deposited in pre-Cambrian time.

Oxidized ore, containing malachite, azurite, and cuprite, extended to a depth of about 400 feet and in its upper part was comparatively rich in gold. Native copper was nowhere abundant. Below the level of complete oxidation there was, according to H. J. Stevens,[1] some chalcocitic enrichment with a relatively high proportion of silver, but I was informed at the mine that the chalcocitic zone was not of great economic importance and soon gave place to primary ore.

COPPEROPOLIS, CALIFORNIA.

The rocks in the vicinity of Copperopolis, Cal., are metamorphosed igneous and sedimentary rocks of the "Bedrock series" and include the Mariposa slate, meta-andesites, and other rocks, cut by gabbro, hornblende, granodiorite, and serpentine.[2] The ore occurs as overlapping lenses, many arranged in echelon, each lens being composed of a complex series of bands or veinlets of chalcopyrite and pyrite deposited mainly parallel to the foliation of the schist. In age the ore, according to Reid, is earlier than the gold-bearing veins of the Mother Lode region. These veins are associated with the acidic intrusives of this part of the Sierra Nevada, which are distinctly later than the copper ore.

The surface zone of oxidized ore is very shallow, 30 feet or less, and a zone of secondary enrichment is entirely lacking. This is no doubt due to the fact that the intense lateral pressure in the rocks has prevented the formation of a vadose circulation. The actual surface is characterized by extensive gossan, in which occur seams of malachite, often very rich, coating the schist. A very small amount of azurite occurs, particularly toward the south. In the Empire ground, south to the concentrator, cuprite is found. Some very rich ore of this kind has been mined within a few feet of the concentrator, to the north. In a small incline shaft, a few feet south of the Empire shaft, cuprite appears as small flakes in the gliding planes of serpentine and talc. The ground to the south, from the Empire shaft to the gabbro boss, shows the largest amount of oxidized ore, due to the greater shattering of the rocks by the latest igneous intrusives.

[1] Stevens, H. J., The Copper Handbook, vol. 9, p. 1369, 1909.

[2] Reid, J. A., The ore deposits of Copperopolis, Calaveras County, Cal.: Econ. Geology, vol. 2, pp. 380–417, 1907.

Beneath this oxidized zone occur the original sulphides—chalcopyrite and pyrite in a gangue of country rock, the latter being usually chlorite schist. The richest ore is pure chalcopyrite; the copper content is lowered both by admixture of pyrite and of country rock. The presence of too much schist or other rock makes a low-grade concentrating ore; too much pyrite produces eventually waste material. Both the sulphide minerals, which occur relatively in all proportions, are found in thin veinlets or bands in the foliation planes of the serpentine and talc.[1]

SHASTA COUNTY, CALIFORNIA.

The copper-bearing region of Shasta County, Cal.,[2] is an area of sedimentary rocks complexly intruded by several varieties of consanguineous igneous rocks. The oldest sedimentary series comprises the Kennett formation (Middle Devonian), which consists chiefly of black fissile shale, with scattered lenses of light-gray limestone and numerous gray or yellowish beds of tuffaceous material. Overlying the Kennett formation unconformably is the Bragdon formation (Mississippian), which consists chiefly of black and gray shales, with thin interbedded layers of tuff and sandstone and bands of conglomerate. Above the Bragdon is the Pit shale, of Middle and Upper Triassic age, consisting chiefly of shales with interbedded layers of volcanic tuff.

The oldest igneous rock is an altered andesite called by Diller the meta-andesite, which underlies and is older than the Kennett and Bragdon formations. A massive, less-altered andesite (Dekkas andesite) overlies the Bragdon and underlies and grades into the Pit. Younger than all these rocks and cutting the latest of them, the Pit shale, are intrusives of soda-rich alaskite porphyry, or soda granite. The alaskite porphyry is cut by quartz diorite, which in turn is cut by acidic and basic dikes that are genetically very closely related to the alaskite porphyry and to the pegmatites of the region. These pegmatites, according to Graton,[3] are more acidic than the present quartz diorite and in places "pass over into siliceous masses that are virtually quartz veins and carry sulphides."

There are two centers of alaskite porphyry, and each is a center of ore deposition.

The important copper deposits consist of large masses of pyritic ore, surrounded in most places by alaskite porphyry, but here and there extending into shale. The ores are of medium richness, yielding at present an average of about 3 to 3½ per cent of copper and $1.50 to $2 per ton in precious metals, generally about equally divided between gold and silver.[4]

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[1] Reid, J. A., The ore deposits of Copperopolis, Calaveras County, Cal.: Econ. Geology, vol. 2, p. 398, 1907.

[2] Diller, J. S., U. S. Geol. Survey Geol. Atlas, Redding folio (No. 138), 1906. Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, pp. 71–111, 1910. Boyle, A. C., jr., The geology and ore deposits of the Bully Hill mining district, California: Am. Inst. Min. Eng. Trans., vol. 48, pp. 67–115, 1915.

[3] Graton, L. C., op. cit., p. 86.

[4] Idem, p. 89.

The ores were probably formed about at the close of the Jurassic or the beginning of the Cretaceous. They are in part replacements in shattered zones of alaskite porphyry which is highly altered by sericitization (soda sericite). The deposits are mineralogically simple. Pyrite is the most abundant ore mineral, and chalcopyrite is the chief one that gives the ores their copper value. Sphalerite or zinc blende is also present in varying amount; on the average it possibly exceeds the chalcopyrite. Some galena is associated with the zinc sulphide, especially in the eastern districts of the region. The gangue minerals are gypsum, calcite, and barite. The minerals which have resulted from the alteration of the primary ore minerals include limonite, magnetite, wad; secondary chalcopyrite, bornite, and chalcocite; cuprite; native copper; small amounts of malachite and azurite; and several sulphates.

In some of the ore bornite, chalcocite, and chalcopyrite are intergrown. The two richer copper sulphides are very commonly intergrown with the chalcopyrite, in places inclosing it and in places being inclosed by it.

These two minerals were found in the deepest workings of the Afterthought mine at a depth of about 600 feet and in the deepest workings of the Bully Hill mine at 970 feet, as well as at higher levels. In places they are intergrown with and even entirely surrounded by barite, and there is no reason whatever to consider them as other than primary constituents of the ore. Both bornite and chalcocite, as well as chalcopyrite, however, are also formed in the upper portions of some of the ore bodies by the process of secondary enrichment, but almost all such occurrences can be readily distinguished from those in which the minerals are of primary origin.[1]

The secondary zone was wonderfully productive of copper and silver at the Iron Mountain and Bully Hill mines, but at other mines it is either of little importance or practically absent. The secondary ores appear to have extended to no great depth and are now exhausted.[2]

SNOWSTORM LODE, COEUR D'ALENE DISTRICT, IDAHO.

The Snownstorm lode,[3] 3½ miles east-northeast of Mullan, Idaho, is a wide zone of impregnation in Revett quartzite (Algonkian) and conforms with the bedding, which strikes N. 60° W. and dips 65° SW. There is no pronounced fissuring along the lode, but microscopic study shows a network of fractures or invisible capillary openings which gave access to the ore-bearing solutions. The vein dips down the slope of the hill, and tunnel 3 is about 800 feet below the surface.

[1] Graton, L. C., op. cit., pp. 104–105.

[2] Graton, L. C., U. S. Geol. Survey Mineral Resources, 1907, pt. 1, p. 599, 1908.

[3] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 151, 1908.

The ore is highly siliceous (over 90 per cent SiO_2) and is in wide demand for use in converter linings. It carried (1904) about 4 per cent copper, 6 ounces silver, and 0.1 ounce gold.

In its unoxidized form the best ore consists of quartzite so crowded with little specks and small irregular bunches of bornite, chalcocite, and chalcopyrite as to be dark gray or nearly black. The microscope shows that the ore minerals to some extent fill irregular microscopic fissures but that for the most part they have replaced the interstitial sericite and siderite of the country quartzite.

Comparatively little of the ore, however, remains in its sulphide condition. Most of it has been oxidized to cuprite and malachite. There is no well-defined zone of oxidation, most of the sulphide ore occurring in No. 2 tunnel [about 460 feet below the outcrop measured on the dip of 65°] and some carbonate in No. 3 tunnel [about 1,200 feet below the outcrop measured on the dip of 65°].[1]

ENCAMPMENT DISTRICT, WYOMING.

The copper deposits of the Encampment district, Wyoming,[2] are in an area of pre-Cambrian metamorphosed igneous and sedimentary rocks, which are cut by pre-Cambrian gabbro, granite, and quartz diorite. The principal mines are the Doane and the Ferris-Haggarty, both of them in fractured quartzite. The primary copper ores are chalcopyrite and pyrrhotite. The secondary ores include azurite, malachite, chrysocolla, bornite, chalcocite, and covellite.

The country is about 10,000 feet above the sea; the climate is moist and ground water is near the surface. The lodes are tight and some mines are dry 450 feet below the surface. At the Ferris-Haggarty mine there was a strong capping of spongy limonite containing no visible copper minerals. At the Doane mine green copper minerals mixed with the limonite were encountered at the surface and continued to a depth of 100 feet or more.[3]

The richest ores occur immediately below the gossan and are composed chiefly of secondary chalcocite.[4] From the position of the stopes in several mine sections some chalcocite appears to extend downward probably 200 feet or more below the top of the chalcocite zone. The secondary copper ores, according to Graton,[5] carried good values in precious metal.

DUCKTOWN, TENNESSEE.

The Ducktown district, in Tennessee, occupies an intermontane basin in the heart of the southern Appalachian region, near the Georgia and North Carolina boundary. The ore deposits outcrop

[1] Ransome, F. L., op. cit., p. 152. The matter in brackets is mine.—W. H. E.

[2] Spencer, A. C., The copper deposits of the Encampment district, Wyoming: U. S. Geol. Survey Prof. Paper 25, 1904.

[3] Idem, p. 45.

[4] Idem, p. 55.

[5] Graton, L. C., U. S. Geol. Survey Mineral Resources, 1906, p. 410, 1907.

between 1,400 and 1,800 feet above sea level. The climate is moist. The prevailing rocks of the district are sandy schists and graywackes, with which are interbedded mica schists. The dominant series is the metamorphosed product of an association of sedimentary beds, including conglomerate, grits, sandstones, and shales. The beds grade into one another along the strike and across the bedding. They contain small bodies of pegmatites and peculiar masses and stringers of an actinolite-feldspar rock which has a composition near that of quartz diorite. The schists are cut by dikes of gabbro, which are not so highly metamorphosed by pressure as the sedimentary beds. The schistosity and the bedding of the sedimentary rocks strike nearly everywhere northeast, and the prevailing dip is southeast. These rocks have been folded into sharp folds, many of them isoclines. Many of the folds were broken along the crests of anticlines[1] and pass into reverse strike faults that nearly everywhere dip southeast.

The ore bodies[2] are replacements of limestone lenses which probably, though not certainly, were deposited at a single stratigraphic horizon. They range in width from a few feet to over 250 feet and have shapes that are characteristic of closely folded sedimentary beds. Anticlines and faulted anticlines, which are characteristic of this region, are shown in the ore zone. The ores themselves are somewhat metamorphosed by dynamic processes, and the gangue minerals are bent and twisted, but at most places they do not exhibit a well-defined schistosity. They were probably deposited after the rock that now incloses them and the limestone they replace had been subjected to considerable dynamic metamorphism. The outcrops are composed of iron oxides and quartz and contrast strongly with the country rock. All the lodes have a general northeast strike. South of the Culchote mine, which is near the center of the productive area, they strike more nearly north than east; north of the Culchote they strike more nearly east than north. In general the lodes dip southeast, but some dip northwest.

The primary ore consists of pyrrhotite, pyrite, chalcopyrite, zinc blende, bornite, specularite, magnetite, actinolite, calcite, tremolite, quartz, pyroxene, garnet, zoisite, chlorite, micas, graphite, titanite, and feldspars. The minerals are generally intergrown and are of contemporaneous age. Essentially the same minerals are found in

[1] Keith, Arthur, U. S. Geol. Survey Geol. Atlas, Nantahala folio (No. 143), 1907.

[2] Safford, J. M., Geology of Tennessee, pp. 469–482, Nashville, 1869. Whitney, J. D., Remarks on * * * the east Tennessee copper mines: Am. Jour. Sci., 2d ser., vol. 20, pp. 53–57, 1855. Ansted, D. T., On the copper lodes of Ducktown, in east Tennessee: Geol. Soc. Quart. Jour., vol. 13, pp. 245–254, 1857. Heinrich, Carl, The Ducktown ore deposits: Am. Inst. Min. Eng. Trans., vol. 25, p. 173, 1896. Kemp, J. F., The deposits of copper ores at Ducktown, Tenn.: Am. Inst. Min. Eng. Trans., vol. 31, pp. 244–265, 1902. Weed, W. H., Types of copper deposits in the southern United States: Am. Inst. Min. Eng. Trans., vol. 30, p. 480, 1901. Emmons, W. H., and Laney, F. B., Preliminary report on the mineral deposits of Ducktown, Tenn.: U. S. Geol. Survey Bull. 470, pp. 151–172, 1911.

all the deposits, but they appear in different proportions at different places in the lodes. Where its content of copper is above 1.5 per cent, or where its sulphur content is high, the material is ore, but where the proportion of actinolite and other lime silicates is greater and the sulphides are less abundant the material, though containing copper and other sulphides, is not workable.

The gossan extends from the surface to a maximum depth of 100 feet. It carries 40 to 50 per cent iron, generally less than 12 per cent silica and alumina, and 0.3 to 0.7 per cent copper. The minerals are hydrous iron oxides, quartz, jasper, and kaolin, with a little cuprite, native copper, and sulphur. Below the gossan iron ores is a zone of dark, rich copper ores, consisting of chalcocite and other copper minerals in a gangue of sulphates, quartz, and decomposed silicates. Under the higher portions of the outcrops of the lodes the top of this zone is about 100 feet below the surface, but the depth decreases down the slopes, and where the lodes are crossed by running streams the secondary copper ores are exposed at the surface. The upper limit of the chalcocite zone follows the level of ground water, which in turn follows the contour of the country, but is less accentuated.[1]

The secondary minerals include argentite, azurite, bornite, chalcanthite, chalcedony, chalcocite, chalcopyrite, chrysocolla, covellite, cuprite, gypsum, iron sulphate, jasper, kaolin, limonite, malachite, marcasite, melaconite, native copper, sulphur, and talc. The copper content of much of this ore ranges from 20 to 30 per cent.

The secondary zone is less extensive vertically than most chalcocite zones elsewhere. The lodes are comparatively impervious to downward circulation, and it is believed that the reactions were brought nearly to completion before the descending oxidized solutions had moved downward great distances.[2] In all the mines except the East Tennessee pyrrhotite is abundant, constituting more than half of the primary ore, and the vertical extent of the chalcocite zone is generally less than 10 feet. In the East Tennessee mine, in which pyrrhotite is much less abundant, the vertical extent of the chalcocite zone is at least 125 feet. The lodes are tight, and the downward circulation was probably slow before the mines were opened, but secondary chalcopyrite has been deposited below the chalcocite zone and probably extends 300 or 400 feet or more below the horizon of chalcocite.

[1] Emmons, W. H., and Laney, F. B., op. cit., p. 170.
[2] Idem, p. 172.

GOSSAN LEAD, VIRGINIA.

The Gossan lead in southwestern Virginia is inclosed in highly metamorphosed crystalline schists. It strikes northeast, dips about 45°, and may be traced almost continuously for 18 miles. It consists of pyrrhotite, chalcopyrite, quartz, hornblende, mica, and other minerals.

Beneath the gossan there is usually found from a foot to 6 feet of the secondary copper ores, containing near the top more or less carbonate and oxide and very rarely a little native copper; farther down, on the top of the unaltered sulphides, there is more or less soft black ore, the so-called "smut ore" of the miners, with secondary chalcopyrite.[1]

As stated by Weed,[2] there has been some postmineral fracturing, which, presumably, would favor a downward circulation. The character of the enrichment is closely similar to that in the pyrrhotite ores at Ducktown, Tenn. As stated by Watson,[3] the weathering measured in 20 operations has extended to an average depth of 34 feet, ranging from 10 to 60 feet.

STONE HILL, ALABAMA.

At Stone Hill, Cleburne County, Ala., a deposit of pyrrhotite, with some chalcopyrite, is inclosed in gneiss and hornblendic and other schists. The ore body is said to be 24 feet wide and is traceable on the surface for 1,200 feet.[4] Below the shallow gossan are rich "black copper" ores of rather slight vertical extent above the yellow sulphides.

ELY, VERMONT.

The copper deposits near Ely, Vt., are lenticular masses in mica schist.[5] Some of the deposits have been worked to very great depths. The ore is composed of pyrrhotite, scattered grains and irregular masses of chalcopyrite, and small amounts of pyrite and zinc blende. The gangue minerals consist of quartz, actinolite, garnet, and other metamorphic minerals. The main part of the ore body consists of very massive pyrrhotite, with small amounts of quartz and other minerals.[6]

The country has been glaciated, and the tops of the deposits have very little gossan, the sulphide appearing at some places at the sur-

[1] Weed, W. H., Copper deposits of the Appalachian States: U. S. Geol. Survey Bull. 455, p. 120, 1911.
[2] Idem, p. 119.
[3] Watson, T. L., Mineral resources of Virginia, p. 421, Lynchburg, 1907.
[4] Weed, W. H., The copper mines of the world, p. 275, New York, 1907.
[5] Smyth, H. L., and Smith, P. S., The copper deposits of Orange County, Vt.: Eng. and Min. Jour., vol. 77, pp. 677–678, 1904. Weed, W. H., Notes on the copper mines of Vermont: U. S. Geol. Survey Bull. 225, p. 190, 1904.
[6] Weed, W. H., op. cit., pp. 192–193.

face. The richer ores near the surface of these deposits were removed long ago, and published descriptions of the details of their occurrence are not available to me. Mr. J. W. Tyson, of the Tennessee Copper Co., at Ducktown, who was present when some of these deposits were opened, informs me that the richer black ores were found within 100 feet of the surface and laid like a floor over the lower-grade yellow sulphides. The relations, he states, were closely similar to those of the "black ores" at Ducktown.

LA DICHA, MEXICO.

The Dicha mine, Guerrero, Mexico, is 150 miles south of the City of Mexico, in a mountainous country about 50 miles east of Acapulco. According to Weed,[1] the ore body, which occurs in micaceous schist, is parallel to the schistosity. It is proved for 7,700 feet along the strike and is from 12 to 88 feet wide. The ore consists of pyrrhotite with streaks, bunches, and specks of chalcopyrite scattered through it. It is said that the primary ore carries 5 per cent copper. Mr. Robert T. Hill[2] informs me that the chalcocite zone is encountered at very shallow depths and is itself very thin, ranging in thickness from 6 inches to 6 feet. Its contact with pyrrhotite is sharp.

SANTIAGO, CUBA.

Copper lodes are found at several places along the south coast of Cuba east and west of Santiago. The most important deposits are those of the El Cobre mine. The ore minerals of the veins include pyrite, chalcopyrite, pyrrhotite, and quartz.[3] Oxidized and chalcocite ores were found 50 or 60 feet below the outcrop. At greater depths pyritic ores in a siliceous gangue were found to carry 6 per cent copper without precious metals in paying quantity. The old workings, now caved, extended 1,300 feet below the surface. Copper is precipitated from mine waters on scrap iron.

PINAR DEL RIO, CUBA.

In the Province of Pinar del Rio, at the extreme west end of Cuba, gossans 150 to 200 feet wide are found. Below the gossans, at depths of 40 to 50 feet, are black copper ores. The sulphides include pyrrhotite, chalcopyrite, and chalcocite.[4] The relations, according to Benjamin B. Lawrence, are similar in some respects to those seen at Ducktown, Tenn.

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[1] Weed, W. H. (quoting R. T. Hill), The copper mines of the world, p. 251, New York, 1907.

[2] Correspondence.

[3] Lawrence, B. B., Copper mining in Cuba: Min. and Sci. Press, vol. 93, p. 602, 1906. Weed, W. H., The copper mines of the world, p. 200, New York, 1907.

[4] Lawrence, B. B., op. cit., p. 602.

QUEEN OF BRONZE MINE, OREGON.

The deposits of the Queen of Bronze mine, in southwestern Oregon,[1] are irregular masses of ore in fractured and fissured portions of gabbro, peridotite, and serpentine.

Although depths of about 300 feet have been reached in the workings, no important body of ore has been found below 125 feet. * * *

The unoxidized ore is chalcopyrite, with which are associated pyrite, pyrrhotite, and subordinate amounts of quartz and calcite. In the low-grade ores pyrite and pyrrhotite are the most abundant minerals. In addition to the copper content, the ores carry some gold and silver.

The oxidized ores are malachite, azurite, cuprite, tenorite (?), and chrysocolla. Of these the black ores containing tenorite or chalcocite are more abundant. The average content in copper was more than 10 per cent. The lower limit of the oxidized ores is usually less than 90 feet from the surface, but some have been found at greater depths. In a small opening about 105 feet below the surface black oxide and small amounts of native copper were observed.[2]

BOUNDARY DISTRICT, BRITISH COLUMBIA.

The Boundary district, British Columbia,[3] lies between Columbia and Okanogan rivers, near the international boundary. The country is mountainous, forested, and about 5,000 feet above sea level. It is an area of sedimentary rocks, including limestones, argillites, and quartzite, with volcanic tuffs and ash beds, probably of Paleozoic age. Associated with these rocks are gneisses and schists, possibly Paleozoic also. The later rocks are porphyries, serpentines, and granodiorite. Various intrusions and flows of andesite, basalt, and other rocks are probably Tertiary. The deposits are perhaps related to intrusions of alkali syenite, which cuts most of the other rocks and is of Tertiary age.

The principal deposits are in limestone or greenstone, not far from intruding masses. The gangue minerals, according to Brock, include garnet, epidote, calcite, quartz, and actinolite. The principal sulphides are pyrite, chalcopyrite, and pyrrhotite. Magnetite is abundant in some deposits, and these contain less of the iron sulphides. Sphalerite, galena, and arsenopyrite are also present, and the ores contain appreciable quantities of gold and silver.

Oxidation extends only a few feet down into the copper ores, and locally the sulphide ore is polished and striated by ice.

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[1] Diller, J. S., and Kay, G. F., Mineral resources of the Grants Pass quadrangle and bordering districts, Oregon: U. S. Geol. Survey Bull. 380, pp. 76–78, 1909. Diller, J. S., Mineral resources of southwestern Oregon: U. S. Geol. Survey Bull. 546, pp. 81–83, 1914.

[2] Diller, J. S., op. cit., pp. 81–82.

[3] Brock, R. W., Preliminary report on the Boundary Creek district, British Columbia: Canada Geol. Survey Summary Rept., 1902, pp. 90–136, 1903. Le Roy, O. E., The geology and ore deposits of Phoenix, Boundary district, British Columbia: Canada Geol. Survey Mem. 21, 1912. Stevens, H. J., The Copper Handbook, vol. 9, pp. 206–207, 1909. Ledoux, A. R., The production of copper in the Boundary district, British Columbia: Canadian Min. Inst. Jour., vol. 5, pp. 171–177, 1902.

The Mother Lode, according to Brock, is over 100 feet wide and at least 1,180 feet long and is developed to a depth of about 500 feet. Chalcocite is practically unknown in this deposit, the principal copper mineral being chalcopyrite. It is reported that the valuable minerals decrease in amount with increase of depth, but it is not certain that the richer deposits near the surface are due to chalcopyrite enrichment. Pay ore, according to Stevens, does not extend below 400 feet. Stevens says that the values have declined from 1.7 per cent copper, 0.5 ounce silver, and $2 gold per ton to about 40 per cent less in copper, 50 per cent in silver, and 60 per cent in gold. The ore reserves in 1910 were estimated by Otto Sussman at 5,595,000 tons.

At Copper Camp, near the head of Copper Creek, oxidized deposits of copper ores are found. In depth these give way to secondary sulphides, including chalcocite, below which are pyrite and chalcopyrite.

On the margins of the principal copper deposits are gold and silver veins. The minerals of these deposits include chalcocite, galena, zinc blende, pyrite, chalcopyrite, ruby silver, argentite, native silver, and gold. The chalcocite, rich silver minerals, and native silver and gold usually occur, it is said, in films around quartz crystals or in small crevices in quartz and calcite, indicating that they are products of enrichment.

VANCOUVER, BRITISH COLUMBIA.

The copper deposits on the west side of Vancouver Island are located near contacts of granite and calcareous sedimentary rocks and are composed of pyrite, bornite, garnet, and other minerals. The ore of the Monitor mine is a mixture of chalcopyrite, pyrrhotite, and coarse magnetite, filling interstices and holding unreplaced rock fragments.[1]

According to William M. Brewer,[2] some of the deposits carry magnetite and gossan at the outcrop, and rich chalcopyrite ore was found in one deposit within 6 feet of the surface.

LA REFORMA MINE, CAMPO MORADO, MEXICO.

The Reforma mine at Campo Morado, Guerrero, Mexico, is in an area of somewhat metamorphosed sedimentary rocks (probably Lower Cretaceous) that are cut by granodiorite, which locally is sheared. Later porphyry, probably monzonite porphyry, intrudes the older rock.

The ore bodies, as stated by J. W. Finch,[3] are large and are extensively developed. The sulphide ore consists of practically solid

[1] Weed, W. H., The copper mines of the world, p. 222, New York, 1907.

[2] Brewer, W. M., The copper deposits of Vancouver Island: Am. Inst. Min. Eng. Trans., vol. 29, pp. 483–488, 1900.

[3] Finch, J. W., A geological journey in Guerrero: Min. and Sci. Press, vol. 101, p. 498, 1910.

masses of pyrite, with chalcopyrite, sphalerite, and galena and little or no quartz. It fills and replaces the beds, usually along the contacts with granodiorite, but is thought to be genetically related to the late intrusions. The Reforma body has an average width on six levels of about 100 feet and is continuous through the mountain. On the sixth level pyrite is developed for 2,000 feet on the strike between the oxidized zone at each end of the level.

The values are about equally distributed between gold, silver, and copper. The pyritic mass is compact and offers no large channels for water circulation. Oxidation is apparently thorough above the water level, but there has been very little reconcentration of copper in the oxidized zone. The copper-bearing waters appear to have drained laterally in the gossan along the strike to the surface or through the footwall slates. The zone of attack of oxidizing agents, as stated by Finch, appears to be measurable vertically in inches along practically all the profile of the pyrite, oxidation being complete as deep as it descends. A little covellite was found at the top of the pyrite in the Navajo workings, near by, but neither covellite nor chalcocite has been recognized in the Reforma. The sulphides appear to be impervious, and there is no evidence whatever of sulphide enrichment.

SAN JOSE, MEXICO.

San Jose, Tamaulipas, Mexico, is 40 miles from Linares, on the Monterey & Mexican Gulf Railway. The principal productive area is about 2,250 feet above sea level. The deposits are in an area of limestone and nepheline syenite, and the limestone is intruded by diorite and by porphyry.[1]

The limestone and the porphyry are cut by tinguaite and by basic dikes. Typical zones of heavy silicates with sulphide copper ores are developed near contacts of limestone and diorite porphyry.[2] Magnetite is a contact mineral and is locally developed in large irregular masses. On the borders there are intermingled garnet and diopside, and throughout the magnetite are abundant veinlets of chalcopyrite and pyrite. One prominent outcrop gave the name "Piedra Imán," or loadstone, to the summit of Remedios Hill.

The most important copper mineral is chalcopyrite, which, according to Kemp, is almost invariably associated with pyrite. They appear not only as inclusions in the silicates but also as veinlets and as coatings in cavities. They cover in places the well-developed crystals of garnet so as to mold around them like a paste. The sulphides may themselves form large masses analogous to the magnetite and thus yield the best stopes of ore.

[1] Finlay, G. I., The geology of the San Jose district, Tamaulipas, Mexico: New York Acad. Sci. Annals, vol. 14, pp. 247–295, 1904. Kemp, J. F., The copper deposits at San Jose, Tamaulipas, Mexico: Am. Inst. Min. Eng. Trans., vol. 36, pp. 178–203, 1906.

[2] Kemp, J. F., op. cit., p. 189.

Ores including malachite, chrysocolla, and subordinate cuprite are found in the oxidized zone, especially along faults. I can find no mention of chalcocite in Kemp's descriptions.

VELARDEÑA DISTRICT, MEXICO.

The Velardeña district, Durango, Mexico,[1] near the Mexican International Railroad, between Torreon and Durango, is an area of folded Mesozoic (probably Cretaceous) limestone, which is covered with andesitic tuffs and flows and cut by andesite intrusions. Dikes and irregular masses of alaskite and of trachytic alaskite and diorite intrude the older rocks. A siliceous phase of the diorite, probably quartz monzonite, is limited to a single intrusion near the Copper Queen mine. Contact metamorphism, with the development of hèavy silicates and metallic sulphides, has attended the intrusion of several of these rocks, and an interesting feature is the metamorphism and development of heavy silicates in igneous as well as in calcareous sedimentary rocks. The ore deposits are of varied character and clearly indicate several epochs of ore deposition.

The deposits differ greatly in mineral composition, but most of them contain considerable zinc blende, zinc being about as abundant as copper. Some deposits contain also pyrrhotite.

The Copper Queen ore body, containing the principal copper ore of the region, consists of three main pipes or chimneys in metamorphic rock at the contact of the Copper Queen intrusion. The principal sulphides are slightly cupriferous pyrite, blende, and galena. The ores here mined are primary and there is no very great change of their nature in depth.[2]

PRINCE WILLIAM SOUND, ALASKA.

The deposits of Prince William Sound, Alaska, are in graywacke and slates[3] of two unconformable series, closely folded but not highly metamorphosed. These are cut by granites, acidic dike rocks, and basic intrusive rocks. Basic flows altered to greenstone are commonly interstratified with the sedimentary rocks. The ores were deposited in zones of fracturing and shearing. The minerals in the ore bodies are chiefly pyrrhotite and chalcopyrite. With these in places are quartz, pyrite, and sphalerite, and at least one vein contains magnetite. As a rule the ore minerals are intimately intergrown and are thus apparently of contemporaneous origin.[4]

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[1] Spurr, J. E., and Garrey, G. H., Ore deposits of the Velardeña district, Mexico: Econ. Geology, vol. 3, pp. 688–725, 1908.

[2] Idem, p. 719.

[3] Grant, U. S., and Higgins, D. F., Reconnaissance of the geology and mineral resources of Prince William Sound, Alaska: U. S. Geol. Survey Bull. 443, p. 20, 1910.

[4] Idem, p. 58.

Possibly extensive surface alteration and sulphide enrichment took place before glaciation, and the remnants of the workable ores may be the roots of such enriched deposits. In the Bonanza mine, Latouche Island, chalcopyrite is less abundant in the lower level than it is nearer the surface. Since glaciation occurred there has been surface leaching and probably enrichment of the deposit, as is shown (1) by gossan, a few feet thick; (2) by a zone of black sulphides, a few inches thick, above the main ore; and (3) by waters that are carrying copper in solution and are in one locality depositing native copper and malachite.[1]

According to F. C. Lincoln[2] the leachings from glacial bowlders have been precipitated in crevices as malachite.

KASAAN PENINSULA, PRINCE OF WALES ISLAND, ALASKA.

The copper deposits of Kasaan Peninsula[3] are in an area of calcareous and other sedimentary rocks, which are interbedded with volcanic tuffs and cut by intruding masses of granodiorite and dikes of granite, syenite, and pegmatite. These intrusions were followed by the intrusion of dikes of felsite and subsequently of small dikes of diabase and basalt, which cut the ore bodies. The sedimentary rocks are greatly metamorphosed near their contact with the intruding rocks, where typical garnet-epidote-magnetite contact zones are developed. The deposits are in the main iron-copper sulphides, intergrown with the garnet gangue, and are generally near the contact of the sedimentary rocks with intrusive syenite. Most of the deposits are worked by open pits.

The ore is composed largely of magnetite, chalcopyrite, and pyrite associated with hornblende and calcite, all of which are included in a more or less banded garnet-epidote gangue.

Surface oxidation has produced considerable limonite and some malachite and azurite; small particles of native copper also occur along slipping planes. These secondary minerals are relatively unimportant.[4]

It appears from descriptions of the mines by Wright and Paige that pyrrhotite and zinc blende are lacking or very subordinate in these deposits. Pyrrhotite occurs in two of the prospects and in one of these zinc blende is present in considerable amount. Chalcocite enrichment is practically absent, though some was noted on the Goodro claims 200 feet below the surface. In the short time since the glacial epoch the pyrite and chalcopyrite have precipitated practi-

[1] Grant, U. S., and Higgins, D. F., op. cit., p. 58.

[2] Lincoln, F. C., The Big Bonanza copper mine, Latouche Island, Alaska: Econ. Geology, vol. 4, p. 212, 1909.

[3] Wright, C. W., and Paige, Sidney, Copper deposits on Kasaan Peninsula, Prince of Wales Island: U. S. Geol. Survey Bull. 345, p. 98, 1908. Wright, F. E. and C. W., The Ketchikan and Wrangell mining districts, Alaska: U. S. Geol. Survey Bull. 347, 1908.

[4] Wright, C. W., and Paige, Sidney, op. cit., p. 105.

cally no secondary copper, though some oxidation has taken place and in a mine at Copper Mountain carbonates were noted 300 feet below the surface.[1]

BONANZA MINE, CHITINA COPPER BELT, ALASKA.

The Chitina copper belt, Alaska,[2] is an area of greenstone, mainly diabase, which is overlain by Triassic limestones. Above the limestones are later sedimentary rocks. The various rocks are cut by quartz diorite porphyry. Andesite and other volcanic rocks, probably of Tertiary age, are also present. The country is rugged and the region of the deposits has been deeply eroded. The principal deposit is a rudely tabular mass of nearly pure chalcocite, which occurs in a fractured or fissured zone in the limestone just above the contact with greenstone. The very rich ore can be traced on the surface for about 250 feet. The deposit carries more than 60 per cent copper and 22 ounces of silver to the ton and in 1908 was estimated to contain 100,000,000 pounds of copper.[3] More recently other very large reserves have been discovered in this region by the Kennicott Mining Co.

In the Bonanza mine the very rich ore, with its included limestone, as seen at the surface, has a width of approximately 25 feet, although the thickness of ore sufficiently rich to be mined may be greater. Below the deposit a little chalcocite and less bornite are found in some of the shearing planes in the greenstone but do not extend far into the greenstone. The quantity of each is small and the minerals are inconspicuous. A small amount of epidote is in places associated with the chalcocite.[4]

Though it extends to the very surface and accumulates in talus from the cliff, the chalcocite ore has no great vertical range. Owing to the rapid mechanical disintegration and the cold climate little or no gossan is developed. Open cavities in the fractured limestone have been filled with ice, and both the country rock and the talus on either side of this ridge are frozen all summer except for a few feet at the surface. Tolman[5] has shown that in the Bonanza mine chalcocite replaces bornite.

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[1] Wright, C. W., Discussion of paper by H. V. Winchell on Prospecting in the North: Min. Mag., vol. 4, p. 359, 1911.

[2] Moffit, F. H., and Maddren, A. G., Mineral resources of the Kotsina-Chitina region, Alaska: U. S. Geol. Survey Bull. 374, p. 80, 1909. Moffit, F. H., and Capps, S. R., Geology and mineral resources of the Nizina district, Alaska: U. S. Geol. Survey Bull. 448, 1911.

[3] Graton, L. C., U. S. Geol. Survey Mineral Resources, 1907, pt. 1, p. 592, 1908.

[4] Moffit, F. H., and Maddren, A. G., op. cit., p. 83.

[5] Tolman, C. F., Observations on certain types of chalcocite and their characteristic etch patterns: Am. Inst. Min. Eng. Bull. 110, pp. 401–408, 1916.

BOLEO, LOWER CALIFORNIA.

The Boleo mines, on the east coast of Lower California, are among the more important copper deposits in Mexico. According to Fuchs,[1] the country is an arid dissected plateau composed of trachytic tuffs and conglomerate, probably Tertiary, which are cut by intrusive trachyte. The ore beds, which conform with the strata, are gently inclined to the sea. There are three beds, each of which is in general from 2 to 8 feet thick, and the three lodes are separated by a few feet of clayey tuffs and conglomerates. The ore beds are altered clayey tuffs and the ore is scattered through the clay in small fragments and nodules, hence the name. The minerals include cuprite, atacamite, azurite, malachite, chrysocolla, crednerite, and salt.

Stevens,[2] who writes later than Fuchs, states that chalcocite and covellite predominate, although the lowest bed, which is partly below the water line, carries oxides and carbonates also. At the bottom of each bed is 6 to 8 inches of rich ore, which was once sorted to run about 20 per cent copper. De Launay[3] supposed that the ores were formed by processes of sedimentation, the mineral waters issuing at the time the volcanic sedimentary rocks were formed, but Weed[4] suggests that they were formed by thermal waters after deposition of the sediments.

BRADEN COPPER MINES, CHILE.

The mines of the Braden Copper Co. are at Rancaqua, in O'Higgins province, Chile, in the Andes. The country rock is andesite surrounding a body of light-gray tuff, which is said to represent the crater of an ancient volcano.[5] The diameter of the volcanic neck is about 4,000 feet and the periphery measures about 2½ miles. It is said to be of Tertiary age, presumably the later Tertiary.

The ore lodes are in and around the periphery of the crater, in andesite at its contact with tuff. The minerals are pyrite, magnetite, chalcopyrite, bornite, secondary chalcopyrite, zinc blende, and tetrahedrite (?). The nonmetallic minerals include tourmaline, quartz, ankerite, calcite, chlorite, sericite, mica, epidote, and zircon. In the zone of oxidation are limonite, cuprite, native copper, and carbonates and silicates of copper.

In one ore body, in the Fortuna mine, chalcocite occurs apparently only as coatings on pyrite and chalcopyrite, increasing the grade of the ore only a little. In the Teniente ore body the effects of sulphide enrichment appear to be somewhat greater. It is concluded, how-

[1] Fuchs, Edmond, Note sur les gisements de cuivre du Boléo: Assoc. franç. avancem. sci. Compt. rend. 14th sess. (Grenoble, 1885), pt. 2, pp. 410–426, 1886.

[2] Stevens, H. J., The Copper Handbook, vol. 9, p. 389, 1909.

[3] Quoted by Weed, W. H., The copper mines of the world, pp. 245–246, New York, 1907.

[4] Idem, p. 246.

[5] Yeatman, Pope, The Braden copper mines: Min. and Sci. Press, vol. 103, pp. 769–772, 1911.

ever, that the copper content is mainly in the primary minerals. Enormous tonnages of ore have been developed, the content of copper being about 2.8 per cent.

NEW LONDON, MARYLAND.

The New London mine, which is about 8½ miles east of Frederick, Md.,[1] is nearly in the center of a long group of exposures of epidote schist, which in turn lies about in the center of a broad belt of phyllites. The ore in the wider parts of the vein consists of coarsely crystalline calcite, quartz, a little barite, and the sulphides chalcocite and bornite. The chalcocite is well crystallized, exhibiting crystal faces exceeding a quarter of an inch in greatest dimensions.

Microscopic examination of polished and etched surfaces of the sulphide ore shows that the bornite commonly occurs between the crystals of chalcocite or occupies fractures in them. Some specimens show a parallel intergrowth of lathlike crystals of bornite and chalcocite. There is no structural indication that the chalcocite has resulted from the replacement of an earlier sulphide, nor is there any evidence that chalcocite has replaced either bornite or pyrite, which are the only other sulphides recognized in the deposit. The coarse crystalline structure of the ore and gangue suggest deep-seated and not surface origin.

The deposit has undergone dynamic metamorphism. Where the vein is narrow and on the borders of its wider parts chlorite, specularite, muscovite, and tourmaline are more abundant, and there is a clearly defined schistose structure. Although the intergrowth of bornite and chalcocite is not graphic, as at Virgilina, there is, as Butler and McCaskey have shown, good evidence that they have not formed as replacements of older minerals.

VIRGILINA DISTRICT, VIRGINIA AND NORTH CAROLINA.[2]

The Virgilina district, in Virginia and North Carolina, is an area of greenstones and sericite schists, cut by granite and gabbro. The intrusive rocks show no schistosity. The schists have been derived from volcanic sedimentary rocks of two types—andesite and quartz porphyry—with tuffs corresponding to these rock types. They are probably of early Paleozoic age.

The veins have a more northerly trend than the schistosity of the country rock. They consist of quartz and, locally and in varying amounts, of epidote and calcite. The ore-bearing veins are confined to the more basic portions of the greenstone schists, and the ore lies in well-defined shoots.

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[1] Butler, B. S., and McCaskey, H. D., Copper ores of the New London mine: Am. Inst. Min. Eng. Trans., vol. 49, pp. 284–291, 1915.

[2] Laney, F. B., The relation of bornite and chalcocite in the copper ores of the Virgilina district of North Carolina and Virginia: U. S. Nat. Mus. Proc., vol. 40, pp. 513–524, 1911.

The ore minerals are bornite and chalcocite. They are chiefly in quartz, but are not confined to any one of the gangué minerals. Bornite is in slight excess over chalcocite and is apparently of only one period of deposition. Chalcocite is of two periods; that of one confined to the upper parts of the vein, younger than the bornite, and filling a network of minute fractures in it; that of the other contemporaneous and in places intergrown "graphically" with it. There is no evidence that any of the bornite is secondary. It is therefore clear, according to Laney, that the greater part of the chalcocite in the Virgilina district is a primary mineral contemporaneous with the bornite.

MOUNT LYELL, TASMANIA.

The Mount Lyell district,[1] near the west coast of Tasmania, includes a narrow belt of schistose rocks (mashed volcanics), which is bordered by an area of quartzitic conglomerates. The ores are confined to the schists and lie along their contact with the conglomerate, the contact being marked by an overthrust fault. Masses of acidic and basic igneous rocks lie near the west coast and within 1½ miles of the deposits. The country has been glaciated.

There are two extensive deposits—the Mount Lyell, a great lens-shaped mass of nearly pure sulphide ore, consisting of pyrite, chalcopyrite, enargite, tetrahedrite, sphalerite, galena, bornite, and chalcocite, and the North Mount Lyell, about a mile north of the Mount Lyell. The North Mount Lyell deposits consist of mineralized belts of schists (fahlbands). The minerals of the ore, named in order of their importance, are bornite, chalcopyrite, chalcocite, tetrahedrite, and pyrite, and these form mineralized zones in the schists. In the dominant type of ore of the North Mount Lyell deposits bornite and chalcocite are in places contemporary; the boundaries between the two minerals are ordinarily intricate and clear-cut, and there are good examples of graphic intergrowths.[2] This structure, according to Gilbert and Pogue, indicates primary chalcocite. Only in a few specimens examined from this district by Gilbert and Pogue was there any evidence of secondary enrichment.

SUDBURY, ONTARIO.

The Sudbury nickel region, Ontario,[3] is in a hilly, glaciated country of low relief. The climate is cold and moist. The nickeliferous

[1] Gregory, J. W., The Mount Lyell mining field, Tasmania, with some account of the geology of other pyritic ore bodies: Australasian Inst. Min. Eng. Trans., vol. 10, pp. 26–196, 1905. Gilbert, C. G., and Pogue, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., vol. 45, pp. 609–625, 1913.

[2] Gilbert, C. G., and Pogue, J. E., op. cit., p. 616.

[3] Barlow, A. E., Report on the origin, geological relations, and composition of the nickel and copper deposits of the Sudbury mining district, Ontario: Canada Geol. Survey Ann. Rept., vol. 14, pt. H, 1904. Coleman, A. P., The Sudbury nickel field: Ontario Bur. Mines Rept., vol. 14, pt. 3, p. 14, 1905.

rocks are included in an elliptical area some 40 miles long and 20 miles wide, the longer axis striking north of east. The central portion of the ellipse, occupied by upper Huronian or post-Huronian rocks, has been weathered to a peneplain, which is surrounded by a hilly belt of eruptive rock. The oldest series in the region consists of Huronian graywacke, slate, quartzite, and conglomerate, which are intruded by acidic and basic eruptives.[1] The upper Huronian rocks (Animikie group) include conglomerate, tuffs, slates, and sandstones. Intruded between the lower Huronian rocks or their igneous intrusives and the upper Huronian sedimentary rocks is the great laccolithic mass, or sheet, probably of Keweenawan age, which constitutes the Sudbury nickel-bearing eruptive. This great sheet dips toward its center, forming a canoe-shaped body which outcrops in a rudely elliptical belt having a nearly plane surface. As a result of magmatic differentiation the lower portion of the eruptive is norite and the upper portion is micropegmatite, the two rocks grading into each other.

The ore deposits are (1) magmatic segregations, which occur between the norite and the underlying rocks, especially in depressions in the Huronian or in rocks intruded in the Huronian; (2) deposits of nearly related genesis in or near dikes of norite that extend outward from the lower contact of the main laccolithic body; and (3) offset deposits outside the laccolith but associated with norite intrusives, which possibly are now connected with the principal body of the nickeliferous eruptive beneath the surface, or which may have connected with the main body before it had been eroded from above the offsets. The ore consists chiefly of pyrrhotite, which contains a small amount of pentlandite and chalcopyrite. At many places it grades imperceptibly into pyrrhotitic norite. Fissures in the eruptive rock are filled with quartz and sulphides, and along the contact with the older rocks sulphides have been deposited by contact-metamorphic processes. Pyrite is intimately associated with some of the pyrrhotite.[2] Other minerals are magnetite, niccolite, cassiterite, gersdorffite, polydymite, danite, galena, native copper, sperrylite, and gold. The gangue includes the rock-making minerals of norite, with some quartz, calcite, and other carbonates. Alteration products include limonite, chalcocite, bornite, morenosite, annabergite, millerite, and probably several other species.

Rounded hills of gossan,[3] indicating the presence of sulphide ore beneath, extend with almost unbroken continuity for miles along the contact of norite with underlying rocks. The offsets and isolated masses of norite with which some of the ore bodies are associated are

[1] Coleman, A. P., op. cit. [2] Barlow, A. E., op. cit., p. 94. [3] Idem, p. 121.

generally made brownish by the decomposition of disseminated sulphides. Locally the covering of gossan is as much as 6 feet deep, although its ordinary depth is 2 or 3 feet, and it merges into sulphide ore beneath. Chalcocite ores are not conspicuously developed, although the presence of chalcocite in some deposits is noted by both Barlow and Coleman. In the Vermilion mine, where the gossan is deepest, chalcocite and copper carbonate are developed and there is a concentration of platinum as sperrylite in the gossan. The relations at the Copper Cliff mine of the Canadian Copper Co. suggest a probable chalcopyrite enrichment. In the earlier years of the development of this mine copper was greatly in excess of nickel, averaging 6.44 per cent, while nickel averaged only 2.38 per cent. Subsequently their proportions were reversed, and in 1904[1] the matte from this deposit contained nearly twice as much nickel as copper. Of sulphide enrichment, C. W. Dickson[2] says that it is possible that the copper disseminated in the upper part of the ore bodies, now eroded, has been secondarily deposited by downward-moving currents, but apparently not to any great extent, for the ground-water level is comparatively near the surface and there is little if any enriched sulphide. When the thin surface covering is removed the pyrrhotite appears perfectly fresh and is without appreciable admixture of secondary minerals, such as are formed in the process of enrichment.

SILVER.

PRINCIPAL SILVER MINERALS.

The chemical composition of the principal silver minerals is given below:

Silver	Ag.
Cerargyrite	$AgCl$.
Bromyrite	$AgBr$.
Embolite	$Ag(Cl, Br)$.
Iodyrite	AgI.
Argentite	Ag_2S.
Pyrargyrite	Ag_3SbS_3 or $3Ag_2S.Sb_2S_3$.
Proustite	Ag_3AsS_3 or $3Ag_2S.As_2S_3$.
Stephanite	Ag_5SbS_4 or $5Ag_2S.Sb_2S_3$.
Polybasite	Ag_9SbS_6 or $9Ag_2S.Sb_2S_3$.
Pearceite	Ag_9AsS_6 or $9Ag_2S.As_2S_3$.
Tetrahedrite (argentiferous)	$4Cu_2S.Sb_2S_3$ or $4(Cu_2Ag_2)S.Sb_2S_3$.
Tennantite (argentiferous)	$4Cu_2S.As_2S_3$ or $4(Cu_2Ag_2)S.As_2S_3$.
Tellurides.	

[1] Barlow, A. E., op. cit., p. 110.

[2] Dickson, C. W., The ore deposits of Sudbury, Ontario: Am. Inst. Min. Eng. Trans., vol. 34, pp. 61–62, 1904.

SOLUBILITIES OF SILVER COMPOUNDS.

The solubilities of several silver salts in water, determined by Kohlrausch,[1] are as follows:

Ag_2SO_4	Ag_2CO_3	$AgNO_3$	AgCl	AgBr	AgI
5.5 .02	0.03 .0001	2134 8.4	0.0016 .00001	0.0001 .0000006	0.000003 .00000001

The upper number in each column shows the number of grams of the anhydrous salt held in solution in a liter of water, the lower number shows the molar solubility—the number of mols contained in 1 liter of the saturated solution at 18° C. A more recent determination[2] of the solubility of Ag_2SO_4 is 7.7 grams per liter at 17° C. The average of four determinations at 25° C. is 8.3 grams per liter.[3] In a water solution saturated with CO_2 at 15° C. 0.846 gram silver carbonate will be dissolved.[4]

NATURE AND RELATIONS OF THE SILVER MINERALS.

Silver, like copper, is dissolved in dilute sulphuric acid, and the solubility of its sulphide, like that of sulphides of copper, is increased by the presence of an oxidizing agent. Like copper, it is precipitated in a reducing environment by metallic sulphides or by hydrogen sulphide. Its sulphide is even less soluble than that of copper. Unlike copper, it does not form stable carbonates, sulphates, or oxides in the oxidizing zone. Its chloride is comparatively insoluble, however, whereas the chlorides of copper dissolve more readily and rarely accumulate as ores. Although ferrous sulphate and copper sulphate are compatible even in solutions of high concentration, ferrous sulphate precipitates metallic silver from a solution of its sulphate. At depths argentite and the silver sulphosalts of antimony and arsenic are precipitated, the latter doubtless in an alkaline environment. As silver is 50 to 100 times as valuable as copper, the natural processes which even slightly enrich silver ores are of great commercial interest.

SOLUTION OF SILVER AS SULPHATE.

Sulphuric acid is a solvent of silver in its sulphide deposits, and as this acid is liberated chiefly by the oxidation of iron sulphides

[1] Determined by the conductivity method. See Smith, Alexander, Introduction to inorganic chemistry, rev. ed., p. 544, New York, 1910.

[2] Euler, Hans, Über Löslichkeitserniedrigung: Zeitschr. physikal. Chemie, vol. 49, p. 314, 1904.

[3] Harkins, W. D., The effect of salts on the solubility of silver salts; V, The solubility of unibivalent salts in solution of salts of different types: Am. Chem. Soc. Jour., vol. 33, p. 1812, 1911.

[4] Johnston, quoted by Seidell, Atherton, Solubilities of inorganic and organic substances, p. 282, 1912.

silver shows little solution and transportation as sulphate in deposits that carry no appreciable iron as sulphide. Such deposits are rare, however, for pyrite occurs in nearly all silver-bearing ore bodies. Silver sulphate, which is only slightly soluble, is formed by the action of concentrated sulphuric acid on silver. Ostwald[1] states that silver sulphate is more soluble in dilute sulphuric acid than in water and that in the reaction an acid salt is probably formed, but, as C. M. Swan[2] has shown, the solubility of silver sulphate is not much increased by the addition of sulphuric acid, if the acid is fairly concentrated. According to H. C. Cooke, silver sulphide is only slightly soluble in very dilute sulphuric acid, but if a little ferric sulphate is added to the solution the solubility of the sulphide is considerably increased.[3] Cooke found also that a little ferric sulphate is almost as effective as a considerable amount and believes that the function of ferric sulphate is to oxidize any hydrogen sulphide that is formed, removing it from the system, in which it would suppress further solution of silver sulphide. According to Vogt[4] ferric sulphate itself will attack metallic silver. Pyrargyrite and polybasite also are dissolved by sulphuric acid, silver and a little antimony going into solution. The reaction, like that with argentite, is greatly increased by the addition of a little ferric sulphate.[5]

The function of ferric sulphate in the oxidizing zone in the solution of silver minerals is indicated by experiments made by Cooke, who took about 1 gram each of natural minerals and of pure artificial minerals and treated them for long periods with solutions (200 cubic centimeters) made by mixing ferric sulphate of about one-twentieth formula weight, marked F in the table below, and sulphuric acid of about one-twentieth formula weight, marked A in the table. The numbers in the first column of the table show proportions of acid and of ferric sulphate in the solutions used. The natural and possibly somewhat impure minerals dissolved a little more rapidly owing, presumably, to their soluble impurities.

[1] Ostwald, Wilhelm, The principles of inorganic chemistry, translated by Alexander Findley, p. 670, London, 1904.

[2] Swan, C. M., quoted by Harkins, W. D., op. cit., p. 1814. The original, a thesis presented to the Massachusetts Institute of Technology in 1899, is not accessible to me.—W. H. E.

[3] Cooke, H. C., The secondary enrichment of silver ores: Jour. Geology, vol. 21, p. 9, 1913.

[4] Vogt, J. H. L., Problems in the geology of ore deposits, in Poĕepný, Franz, The genesis of ore deposits, p. 677, 1902.

[5] Cooke, H. C., op. cit., p. 11.

Solution of silver minerals in sulphuric acid and ferric sulphate.

Solution.	Mineral.	Loss of weight.	Time.	Remarks.
		Gram.	*Days.*	
Water	Argentite	0.0010	98	
A	do	.0019	98	
A:F::3:1	do	.0062	98	
A:F::1:3	do	.0074	98	
Water	Pyrargyrite	.0111	101	
A	do	.0093	101	
A:F::3:1	do	.0120	101	
A:F::1:1	do	.0125	101	
A:F::1:3	do	.0144	101	
Water	Stibnite	.0175	84	Weights give weight of Sb_2O_4 obtained from analysis of solutions.
A	do	.0205	84	
A:F::3:1	do	.0185	84	
A:F::1:3	do	.0160	84	
F	Silver chloride	.....	33	Solutions gave no Ag.
F:H_2O::1:1	do	.0000	33	
N/5 H_2SO_4	do	.0000	33	

The following experiments by Cooke,[1] made to test the solubility of metallic silver in various solutions of salts contained in mine waters, likewise show the degree of efficiency of ferric sulphate as a solvent. Small pieces of leaf silver (2 square centimeters in area) were corked in tubes containing 75 cubic centimeters of solution and left in the dark 73 days at 22° C. When chloride formed it was removed before weighing. The loss of weight of silver in grams is shown below. The values of A and F are given above (p. 253).

Solution of metallic silver.

Solution:	
N/10 NaCl	0.00000
N/10 NaCl: N/10 H_2SO_4: : 1:1+MnO_2	.01538
N/10 HCl	.04502
N/10 H_2SO_4	.00019
A:F::1:1	.08252

It is noteworthy that ferric sulphate increases the solubility of native metal in sulphuric acid more than a hundredfold. Manganese oxide likewise increases its solubility, even in the presence of chloride, which forms with silver a nearly insoluble salt, silver chloride, AgCl. Cooke ascribes the solvent action shown in the table to the presence of air, which sets up an oxidation potential between the silver and the solution and aids in the solution of the silver. He believes that acids can not attack silver directly in the absence of any oxidizing agent, as the solution tension of the silver is less than that of the hydrogen which would be given off.[2] This may account for the moderate stability of native silver in the zone below that where oxidation is most active.

[1] Cooke, H. C., op. cit., p. 12. [2] Idem, p. 15.

It is stated above that silver sulphate is more soluble in sulphuric acid than in water. In this connection Harkins's experiments[1] indicate the presence of a complex ion of silver. Silver sulphate is said to ionize as follows—

$$\frac{[Ag]^2 \times [SO_4]}{Ag_2SO_4} = \text{a constant}$$

One would suppose that by adding sulphuric acid or ferric sulphate—that is, by adding more SO_4 ions—the quantity of silver in solution would be rapidly reduced, in accordance with the rule of the solubility product. But the reverse happens; that is, when sulphuric acid is added more silver goes into solution. Moreover, as ferric sulphate is increased the amount of silver that may be held in solution is slowly but steadily increased. Cooke suggests that the silver is present as part of the ion $AgSO_4^-$, the solubility of which would not be affected by the presence of the SO_4 ion.[2]

The reaction of sulphuric acid and argentite is

$$Ag_2S + H_2SO_4 = Ag_2SO_4 + H_2S.$$

Cooke believes that the reaction is brought to equilibrium as soon as only a little hydrogen sulphide is formed. The oxygen of the air will remove hydrogen sulphide, but not enough to allow the reaction to proceed far. On the other hand, ferric sulphate removes the hydrogen sulphide quickly and completely, as follows:

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S.$$

Silver oxide could not accumulate in oxidizing zones, because it is soluble in acid and also in water to the extent of 0.021 gram silver oxide in a liter of water at 20°.[3] It is unknown as a natural mineral.

SOLUTION OF SILVER AS CHLORIDE.

Notwithstanding the low solubilities of the silver halides and the nearly universal occurrence of chlorine in mineral waters, it seldom happens that all the silver dissolved in the upper parts of an argentiferous deposit is fixed as halides. The formation of the chloride near the surface does not entirely inhibit the downward migration of silver. The secondary silver sulphides are numerous and in some veins abundant. The reasons for the fairly extensive downward migration of silver, even where chlorides are formed, are:

1. Chlorides are present in the natural waters in some deposits in amounts insufficient to precipitate as chloride all the silver that goes into solution as sulphate.

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[1] Harkins, W. D., Am. Chem. Soc. Jour., vol. 33, p. 1836, 1911.
[2] Cooke, H. C., op. cit., p. 16.
[3] Seidell, Atherton, Solubilities of inorganic and organic substances, p. 289, 1912.

2. Silver chloride is itself slightly soluble in water.

3. Silver chloride and other halides of silver are soluble in an excess of alkali chlorides.

From this it follows that if a silver solution in the upper part of a deposit contains a certain small amount of alkali chlorides some of the silver will be fixed as chloride; but if it contains sufficient alkali chloride horn silver will be dissolved and will migrate downward with other metals. That some silver is held in solutions containing both sulphates and chlorides is shown by an analysis of mine water reported by Reid.[1]

According to Barlow[2] a water solution of sodium chloride containing 34.3 grams per liter will dissolve only 0.0018 gram silver chloride at 20° C. Lower concentrations dissolve even less. Since, as stated on page 252, water dissolves 0.0016 gram silver chloride per liter at 18°, it is obvious that the addition of sodium chloride to a silver chloride solution will reduce the concentration of silver to a minute quantity. The amount of silver chloride in solution increases to 0.0018 gram per liter only when the amount of sodium chloride present is increased to 34.3 grams per liter. Thereafter it increases proportionally much faster than does the concentration of sodium chloride; hence, as pointed out by Cooke,[3] it is probable that in sodium chloride solutions of strength less than 34.3 grams per liter the concentration of silver will never be more than about the amount dissolved in pure water, but usually less.

These data show that only when the amount of sodium chloride exceeds 34.3 grams per liter will mineral waters be solvents superior to those in which chlorides are absent. Such concentrations rarely occur in waters that leach silver deposits. Because the addition of sodium chloride in quantities that exist in mineral waters makes cerargyrite less soluble, the chloride waters of arid regions render cerargyrite more stable. It is in such regions that cerargyrite is most abundant.

The order of the solubility of the chloride, the bromide, and the iodide of silver are expressed by the order in which they are here named. All of them are very sparingly soluble in water; consequently the halogens will precipitate silver from sulphate solutions and the halides may remain in the upper portions of deposits, giving a considerable enrichment at or near the surface. A cold solution of a bromide will slowly convert the precipitate of silver chloride into bromide, and a soluble iodide will similarly transform the bromide or the chloride into iodide. If the three halogens were equally abundant

[1] Reid, J. A., The structure and genesis of the Comstock lode: California Univ. Dept. Geology Bull., vol. 4, pp. 189–190, 1906.

[2] Barlow, W. E., The solubility of silver chloride in hydrochloric acid and in sodium chloride solutions: Am. Chem. Soc. Jour., vol. 2, p. 1446, 1906.

[3] Cooke, H. C., op. cit., p. 20.

in mine waters, the bromide and iodide of silver would probably predominate in the silver deposits, but chlorine only is abundant. Consequently cerargyrite, AgCl, is much more common than embolite, Ag(Cl,Br); bromyrite, AgBr; iodobromite, Ag(Cl,Br,I); and iodyrite, AgI.

If, in a solution containing the three halogens, chlorides are vastly in excess, silver chloride will be precipitated first, even if bromides and iodides are present, for in mixed solution the least soluble salts are not precipitated first if a more soluble salt is present in sufficiently greater concentration.

The relations of the halides of silver at Tonopah, Nev., should be mentioned in this connection. According to Burgess,[1] the silver halides at some places occupy fairly well marked horizons in the altered veins. The chloride, cerargyrite, occupies the upper zone, embolite the middle zone, and iodyrite the lower zone. The zones are usually not distinct, and in places two of the minerals are found together. Of these relations Burgess says:

> The order of crystallization was chloride, bromochloride, iodide, which is contrary to what would be expected from their respective solubilities, since iodide is the least soluble and would be expected to precipitate first. * * * The most obvious explanation seems to be that the chloride was precipitated first because of the great excess of alkaline chlorides in the solution, and that as the chlorine became reduced in quantity it was partly replaced by bromine, and that the iodide was formed only after the concentration of the other halogens was considerably reduced.

SOLUTION OF SILVER AS CARBONATE.

The carbonate of silver, as shown in the table on page 252, is fairly insoluble. Yet it is more soluble than any natural silver salt except the sulphate. With excess of carbon dioxide under moderate pressure the solubility of silver carbonate is considerably increased. This may reach a point where the carbonate becomes an effective carrier of silver. Little experimental data on this matter are available, yet the relatively great depth to which silver, compared with gold, is carried downward in deposits where calcite and other carbonates abound suggests that the carbonate is an agent of transportation. Ravicz has shown that calcite, siderite, and rhodochrosite do not precipitate silver from moderately dilute solutions of carbonate or sulphate of silver.[2]

PRECIPITATION OF SILVER.

Silver is precipitated in many ways—by decrease in acidity of the solution, by decrease in the state of oxidation of the solution (that

[1] Burgess, J. A., The halogen salts of silver and associated minerals at Tonopah, Nev.: Econ. Geology, vol. 6, p. 13, 1911.

[2] Ravicz, L. G., Enrichment of silver ores: Econ. Geology, vol. 10, pp. 368–392, 1915.

is, by the accumulation of "ous" salts, particularly of ferrous sulphate), or by contact with certain minerals that precipitate the native metal. The table below shows the results obtained by Palmer and Bastin[1] in solutions of silver sulphate, about one-fortieth normal, and by Grout[2] in dilute solution of sulphuric acid and silver sulphate.

Order of reactivity of minerals precipitating silver from water solutions of silver sulphate (column 1) and from dilute solutions of sulphuric acid and silver sulphate (column 2).

	1	2
Alabandite	Strong	Very strong.
Niccolite	Very strong	Do.
Tetrahedrite		Strong.
Covellite	Strong	
(Siderite)		Weak.
Cobaltite	Strong	
Smaltite	Moderate	Very strong.
Pyrrhotite	do	Strong.
Arsenopyrite	do	Do.
(Cuprite)		Do.
Molybdenite		Weak.
Millerite	Weak	Do.
Galena	do	Do.
Chalcocite	Very strong	Strong.
Bornite	Strong	Do.
Jamesonite	Weak	
Enargite	Strong	Moderate.
Marcasite	Moderate	Weak.
Tennantite	Strong	Very strong.
Black jack		Weak.
Stannite		Strong.
Orpiment	Weak	Weak.
Pyrite	do	Do.
Rosin jack	do	Do.
Cinnabar	do	Do.
Stibnite	do	Do.
Chalcopyrite	Moderate	Do.
Realgar	Weak	Moderate.
(Ferrous silicates, etc.)		Weak.

The cuprous minerals cuprite, chalcocite, and enargite remove silver from solution more rapidly even than they remove gold. The reaction with chalcocite[3] may be expressed as follows:

$$Cu_2S+2Ag_2SO_4=2CuSO_4+Ag_2S+2Ag.$$

The precipitation of silver is not retarded by the presence of a large excess of copper sulphate or by the presence of zinc sulphate. This reaction with chalcocite will go on also in the presence of ferric sulphate. Galena also will precipitate some silver. In lead-silver ores the galena is generally richer in silver in the oxidized zone than at greater depths. In a Leadville mine, according to Ricketts,[4] the average content of galena is 180 ounces to the ton, whereas

[1] Palmer, Chase, and Bastin, E. S., Metallic minerals as precipitants of silver and gold: Econ. Geology, vol. 8, p. 140, 1913.

[2] Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, pp. 407–433, 1913.

[3] Palmer, Chase, and Bastin, E. S., op. cit.

[4] Ricketts, L. D., The ores of Leadville, pp. 32, 38, Princeton, 1883.

the cerusite around the cavities in the galena carries only 50 ounces or less to the ton.

Kaolin and orthoclase[1] also, as shown by Sullivan, will slowly precipitate silver from solution. As pointed out by Grout,[2] carbonates will precipitate native silver after they have nearly neutralized the solution by forming inert sulphates. This recalls to mind the native silver found in cleavage cracks of calcite in the Cobalt district[3] of Ontario and deposits at Batopilas, Mexico, where, according to Collins,[4] native silver occurs invariably in calcite. As already stated the carbonates do not precipitate all of the silver, and if the solution is sufficiently dilute none is precipitated. Organic or carbonaceous matter also readily precipitates silver from its solutions.[5]

Ferrous sulphate will precipitate silver from solutions of sulphuric acid and ferric sulphate in which silver is present as sulphate. This subject has recently been investigated at considerable length by H. C. Cooke. As ferrous salt increases and ferric salt decreases the silver held in solution decreases, and with only ferrous sulphate in solution all the silver is precipitated, as is shown by the table below, which is a rearranged abridgment of a table prepared by Cooke.[6] The figures indicate concentrations in formula weights per liter.

Equilibrium between ferric, ferrous, and silver sulphates.

$Fe_2(SO_4)_3$.	$FeSO_4$.	Ag_2SO_4.
0.00749	0.01094	0.004200
.00737	.01406	.003226
.00695	.01849	.002294
.00626	.02451	.001298
.00370	.03972	.000439

With these and other values of these systems, Cooke has proved the following relation:

$$\frac{CFe'''}{CFe''\times CAg'}=163\pm$$

[1] Sullivan, E. C., Interaction of minerals and water solutions: U. S. Geol. Survey Bull. 312, pp. 37–64, 1907.

[2] Grout, F. F., op. cit., p. 418.

[3] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, 1913. (See particularly the photograph on p. 14.)

[4] Collins, H. F., Deep mining in Mexico: Inst. Min. and Met. Trans., vol. 3, p. 441, London, 1895.

[5] Senarmont, H. de, Annales chimie et phys., 3d ser., vol. 32, p. 140, 1851. Rickard, T. A., The formation of bonanzas in the upper parts of gold veins: Am. Inst. Min. Eng. Trans., vol. 26, p. 978, 1896.

[6] Cooke, H. C., The secondary enrichment of silver ores: Jour. Geology, vol. 21, p. 18, 1913.

where CFe'''=concentration of ferric ion in solution, CFe''=concentration of ferrous ion in solution, CAg'=concentration of silver ion in solution.

A decrease of ferric or increase of ferrous ion therefore rapidly decreases the quantity of silver in solution. Grout[1] has shown, moreover, that ferric sulphate will inhibit the precipitation of silver from its sulphate solutions in contact with many sulphides that readily precipitate silver in the absence of ferric sulphate.

Hydrogen sulphide and alkaline sulphides precipitate silver as sulphide from acid solutions. Below the zone of oxidation silver is readily precipitated as argentite on account of the low solubility of the sulphide—0.552×10^{-6} mols per liter.[2] Silver stands near the end of the Schuermann series, being preceded only by mercury, and accordingly it should replace most other metals in sulphide combinations. With silver sulphate (Ag_2SO_4) hydrogen sulphide (which is generated by acid reacting upon zinc blende, galena, or other sulphides) gives argentite, which is one of the most important silver minerals in ores. The reaction is

$$Ag_2SO_4+H_2S=Ag_2S+H_2SO_4.$$

If the reaction is with galena, or if lead sulphide is precipitated simultaneously with argentite, argentiferous galena may be formed.

In zones nearer the surface of the earth, where ferric sulphate is present, any hydrogen sulphide generated by the action of acid on sulphides is immediately oxidized, probably according to the equation

$$Fe_2(SO_4)_3+H_2S=2FeSO_4+S+H_2SO_4.$$

As ferric sulphate is eliminated the conditions become increasingly favorable for the accumulation of hydrogen sulphide, and with silver sulphate argentite is precipitated. The sulphur that was set free by the reduction of ferric sulphate can react with native silver, forming argentite:

$$2Ag+S=Ag_2S.$$

This synthesis was made experimentally by H. C. Cooke.[3] An acid solution of ferric sulphate was partially reduced to ferrous salt by passing in hydrogen sulphide,[4] after which it was allowed to stand for a few minutes in order that all the hydrogen sulphide in solution

[1] Grout, F. F., op. cit., p. 420.

[2] Weigel, Oskar, Die Löslichkeit von Schwermetallsulfiden in reinem Wasser: Zeitschr. physikal. Chemie, vol. 58, p. 294, 1907.

[3] Op. cit., p. 25.

[4] Brownlee, R. H., On precipitated sulphur: Am. Chem. Soc. Jour., vol. 29, p. 103, 1907.

might be used up. Some silver previously precipitated by reaction of ferrous sulphate with silver sulphate was then added. Reaction did not occur at once, but at the end of 24 hours all of the silver had been altered from silvery white flakes to black silver sulphide.

Up to this point the chemistry of the enrichment of silver ore is clear. In the upper zones silver goes into solution as sulphate and subordinately as chloride and carbonate and is precipitated as native metal where ferric sulphate is eliminated. Again, native metal will pass into solution until ferrous sulphate has accumulated to a moderate concentration. In the lower zones argentite can form even in the presence of acid, and in the absence of ferric salt or other source of oxygen it is highly stable. The complex arsenic and antimony sulphosalts are formed in and at some places below the zone where argentite forms. The conditions that exist where these salts form are not well known, but some experiments have shown the syntheses of the salts under natural conditions. H. C. Cooke[1] powdered stibnite, passed it through an 80-mesh screen, and covered the powder with a solution of silver sulphate about one-thirtieth normal. After 36 days the stibnite contained 1.3 per cent silver. Similarly realgar and orpiment that had been passed through a 40-mesh screen were covered with one-fortieth normal solution of silver nitrate. After 68 days the realgar contained 1.9 per cent and orpiment 9.8 per cent silver. The nature of the silver minerals, however, can not be stated.

That both arsenic and antimony are dissolved in underground waters is indicated by the removal of compounds containing these elements in the oxidized zones and gossans of deposits which at greater depths carry them, by their presence in small amounts in mine waters and by their solution in experiments in which their minerals are treated with dilute alkalies.

It is generally supposed that most compounds of arsenic and antimony may be either primary or secondary. The data now available indicate that pyrargyrite and proustite are nearly everywhere secondary minerals; that stephanite, polybasite, and pearceite are secondary in most of their occurrences; that tetrahedrite and tennantite, which frequently contain silver as well as copper, are in general primary. The two minerals last named are found at some places in cracks that cut the primary ore, and in a few places it is clear that their occurrence is related to the present topographic surface.

In the subjoined table the more important antimony sulphosalts of silver are put in the first column, the arsenic sulphosalts in the

[1] Op. cit., p. 24.

second. Tetrahedrite and tennantite are included, for they are commonly argentiferous.

Rather common.	Rare.
Pyrargyrite=$3Ag_2S.Sb_2S_3$.	Proustite=$3Ag_2S.As_2S_3$.
Tetrahedrite=$4Cu_2S.Sb_2S_3$.	Tennantite=$4Cu_2S.As_2S_3$.
Stephanite=$5Ag_2S.Sb_2S_3$.	
Polybasite=$9Ag_2S.Sb_2S_3$.	Pearceite=$9Ag_2S.As_2S_3$.

The minerals in the first column are, as a rule, much more abundant and they are of commoner occurrence than the corresponding minerals in the second column. Proustite is probably less common and less abundant than pyrargyrite, tennantite less common and less abundant than tetrahedrite. Polybasite is not an uncommon mineral, but pearceite has been identified at only a few places. If the antimony sulphosalts, where secondary, have been deposited mainly as results of reactions of silver-bearing sulphate waters on stibnite, it would appear that arsenic minerals are less common than the antimony minerals or else that they are less readily replaced under the conditions that exist in veins. But arsenic is in fact as abundant in ore deposits as antimony and is much more readily dissolved in acid solutions. These relations and many others suggest that the complex antimony and arsenic sulphosalts of silver are formed in an alkaline environment. In such an environment arsenic and antimony sulphides are very readily dissolved. L. G. Ravicz[1] has shown that pyrargyrite is about one-tenth as soluble in alkaline solutions as proustite and therefore could be more readily precipitated from dilute solutions.

That the double sulphides of silver are formed in alkaline solution is strongly suggested also by the work of Grout. Stibnite was treated with a 1 per cent solution of sodium carbonate and to the resulting filtrate various amounts of silver sulphate were added. The precipitates analyzed were as follows:[2]

Analyses of precipitates obtained from mixture of acid solutions with silver sulphate and alkaline solutions of antimony sulphide.

[Quantities in grams.]

Mixture used.		Precipitate obtained.	
Silver sulphate.	Antimony sulphide.	Ag_2S.	Sb_2S_3.
0.0083	0.0050	0.0066	0.0032
.0415	.0050	.0095	.0025
.0830	.0050	.0097	.0024
.1660	.0050	.0100	.0024

[1] Ravicz, L. G., Experiments in the enrichment of silver ores: Econ. Geology, vol. 10, pp. 378–384, 1915.

[2] Grout, F. F., op. cit., p. 429.

Wherever silver is present both metals are precipitated and considerable antimony is precipitated when the silver is present in excess. When there is enough or more than enough silver present to unite with the antimony the analyses of precipitates above indicate approximately the composition of stephanite $(Ag_2S)_5.Sb_2S_3$. The reaction may be written:

$$5Na_2S.Sb_2S_3+5Ag_2SO_4=5Na_2SO_4+(Ag_2S)_5.Sb_2S_3.$$

In the reactions where argentite and the complex sulphosalts are formed ferric sulphate is probably not present. Certainly it is not used up by hydrolysis to form ferric hydroxide, for iron oxide is rarely associated with argentite, pyrargyrite, and other secondary silver sulphides that are formed in depths below the zone of active oxidation. The elimination of a little ferric sulphate that might be present when argentite forms does not take place by hydrolysis, for in that case iron oxides would be present with the secondary silver minerals; but reduction of ferric iron may take place through the agency of hydrogen sulphide or alkaline sulphides:

$$Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S.$$

TRANSPORTATION OF SILVER AND DEPTH OF SECONDARY ORE IN SILVER DEPOSITS.

In view of the facts that silver sulphate is moderately soluble and that native silver is readily precipitated from solutions of silver sulphate by so many natural and abundant substances, it is noteworthy that in many well-known mining districts there is very little of the native metal. In some districts it is a valuable ore mineral; in others it is exceedingly rare, notwithstanding the fact that the conditions appear to be favorable to its formation. (See p. 258.) In many regions it is mainly a transition product, which is subsequently dissolved and reprecipitated at greater depths. Silver is doubtless carried downward by stages, repeatedly going into solution and being precipitated until it finally reaches an environment where it is more stable, either as native silver or as argentite, or as one of the complex silver salts. As depth increases the conditions become more and more favorable to its stability (1) by increase of ferrous and decrease of ferric sulphate, (2) by decrease of acidity, (3) by generation of hydrogen sulphide and alkaline sulphides.

Any native silver or argentite that has been precipitated near the surface will be redissolved so long as ferric sulphate is present. The native metal can be dissolved in minute amounts even in a solution that contains only a trace of ferric iron. When all the ferric salt is used up the solution as sulphate practically stops.

Though there is no invariable rule respecting the relations of the silver chloride, the native metal, the sulphide, and the arsenic and antimony sulphosalts in deposits containing all these minerals, yet in many deposits these minerals have fairly well defined horizons. The chloride is most abundantly developed above the argentite ore; the antimony and arsenic sulphosalts are found at depths below the zone where argentite is most abundant, but some argentite also is found with them. The native metal is found with the chloride, and, overlapping the zone of chloride ores, it extends downward with argentite. In the Granite-Bimetallic mine, at Philipsburg, Mont., the deeper secondary ores contain very little argentite or native metal, the richer minerals being almost exclusively the dark and the light ruby silver. At Georgetown, Colo., according to Spurr, Garrey, and Ball, argentite predominates in the upper part of the secondary sulphide zones, and the secondary arsenic and antimony sulphosilver minerals are more important below the argentite zone. At the Banner[1] mine, in the Silver City mining district, Owyhee County, Idaho, rich shoots of argentite in a gangue of quartz and kaolin were mined in the upper workings. At increased depth the argentite was succeeded by pyrargyrite and other sulphosalts of silver.

No limit can be definitely set to the depth to which silver is carried downward, but a few examples are noteworthy. At Ducktown, in heavy pyrrhotite ores, practically all the secondary silver was concentrated within 100 feet of the surface. In the copper mines at Butte, Mont., where iron sulphides abound, the silver was concentrated mainly in the oxidized ore as the native metal and in general lies not more than 200 to 400 feet below the surface, but locally it was found deeper. Pearce[2] mentions rich argentiferous sulphides that may be secondary on the 500-foot level of the Gagnon mine. At the Yankee Girl mine, between Silverton and Ouray, Colo., the rich silver ores extended to depths of 600 or 700 feet, where they changed to low-grade pyritous ore. The best ore in the silver deposits at Georgetown, Colo., is within 500 feet of the surface, although good ore extends to depths of 700 or 800 feet, and, exceptionally, 1,000 feet. At Breckenridge, Colo., operations in general were not profitable below the depth of 300 or 350 feet. At Lake City, Colo., the best ore is within 300 or 400 feet of the surface, but in some deposits, such as those in the Moro mine, secondary sulphides are found nearly 500 feet vertically below the surface. At the Granite-Bimetallic mine, Philipsburg, Mont., nearly all the secondary ore is within 1,000 feet and most of it within 700 feet of the surface. At Creede, Colo., there is

[1] Ravicz, L. G., oral communication.

[2] Pearce, Richard, The association of minerals in the Gagnon mine, Butte City, Mont.: Am. Inst. Min. Eng. Trans., vol. 16, p. 63, 1888.

clear evidence of some secondary enrichment of silver at a depth of 1,100 feet, but nearly all the rich ore is within 700 feet of the surface. At Aspen, Colo., rich ore, with native silver, is found as deep as 900 feet below the surface. At Tonopah, Nev., good ore, probably in part secondary, is found about 1,000 feet below the surface, and perhaps at greater depths. On the Comstock Lode there is clear evidence of secondary concentration, and good ore is found below depths of 1,000 feet, but no exact data on this point are available. The richest deposits, however, were found within 1,000 feet of the surface. In the St. Eugene mine, Moyie, British Columbia, where there are strong indications of sulphide enrichment, the workable ore appears to be confined to depths within about 800 feet of the surface.

INFLUENCE OF MINERAL COMPOSITION ON DEPTH OF SECONDARY BONANZAS IN SILVER DEPOSITS.

Some silver deposits were formed near the surface and were doubtless originally richer in their superficial parts. It is difficult to determine to what extent these deposits owe their bonanzas to weathering and downward enrichment. Other silver deposits—for example, those of the Granite-Bimetallic mine at Philipsburg, Mont.—were formed a mile or more below the surface,[1] and plainly owe their rich ores to secondary enrichment. Moreover, many regions, particularly in Colorado, have been deeply dissected since the ores found in them were formed, and the relation of the rich ores to the present surface does not indicate their relation to the surface that existed when the primary ores were formed. In general, where primary ores are extensively fractured, secondary ores lie at greater depths. In all the regions named above, where secondary ores are found at considerable depths, the primary ore is greatly fractured.

In view of the rapidity with which certain minerals decrease acidity and reduce ferric to ferrous iron, one would suppose that deposits which contain such minerals in large quantities would be enriched to shallower depths than deposits which contain only the more nearly inert minerals. Thus deposits containing much pyrrhotite would precipitate silver rapidly, and the accumulation of ferrous sulphate in them would prevent the re-solution and downward transfer of the silver. Pyrrhotite is probably the most active common mineral as a precipitant of silver. Certain minerals may be grouped as indicated below, in the order of their reactivity:

1. Pyrrhotite, chalcocite, enargite, the alkali-rich silicates, leucite and nepheline, and the iron silicates, olivine, augite, and hornblende.

[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 188, 1913.

2. Galena and sphalerite, and the gangue minerals fluorite, biotite, and orthoclase.

3. Pyrite, chalcopyrite, quartz, and muscovite.

Deposits composed of the minerals of groups 2 and 3, other conditions being equal, should be more deeply enriched than deposits containing appreciable quantities of pyrrhotite or other minerals of group 1, and the enrichment would not be concentrated in so small a vertical range. Very few silver deposits contain minerals of group 1 in large amount, but silver is present in some copper ores of that type. In the pyrrhotite ores of Ducktown, Tenn., silver was concentrated within not more than 100 feet of the surface and in a vertical zone 10 feet thick or less. In the ores of the Monte Cristo district, Washington, which carry pyrrhotite, enrichment is also shallow. Most silver deposits contain some of the minerals of group 2. Such combinations would cause precipitation at moderate rates and enrichment at intermediate depths, unless some minerals of group 1 also were present.

The effect exerted on silver solutions by carbonates in the gangue has been noted. Recent experiments of Ravicz[1] show that silver is not precipitated from very dilute silver sulphate solutions by calcite, siderite, or rhodochrosite. If a solution of silver sulphate is acid they will neutralize it, but carbon dioxide is released and the silver remains in solution, probably as bicarbonate. Even alkali carbonates do not remove all the silver from solution. But metallic sulphides in the presence of carbonates will precipitate the silver, the ones noted as efficient (pyrrhotite, chalcocite, and others) acting more rapidly than the inert sulphides, such as pyrite.

As between silver and gold in calcitic deposits silver is carried deeper. The silver deposits of the Comstock lode, of Tonopah, of the Georgetown region, Colorado, and of several other districts, show enrichment at moderately great depths, though the ores or altered wall rocks generally contain appreciable carbonates. Silver carbonate is much more soluble than copper carbonate. Its high solubility would favor the downward transportation of silver where silver is carried as carbonate.

OUTCROPS.

The outcrops of silver deposits may carry silver in concentrated form or they may be partly leached of the metal. If the leaching waters carry much chloride, silver may be greatly concentrated at the outcrops, particularly in arid and semiarid countries,[2] where

[1] Ravicz, L. G., Experiments in the enrichment of silver ores: Econ. Geology, vol. 10, pp. 368–392, 1915.

[2] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 314, 1892.

the waters of undrained basins may supply abundant sodium chloride and where dust that contains chloride may be carried and scattered by the winds. The chlorides not only supply chlorine for the precipitation of silver, but suppress the solution of silver chloride in

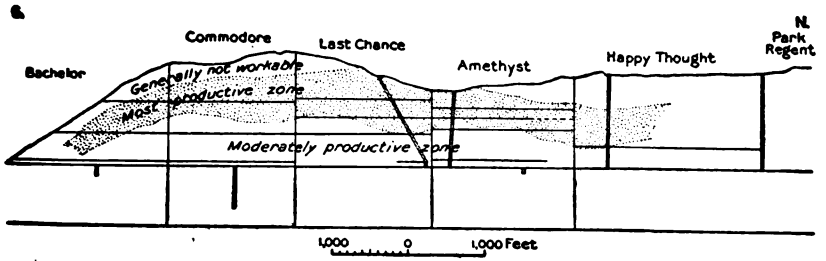

FIGURE 16.—Longitudinal or vertical projection of the Amethyst lode, Creede, Colo. After W. H. Emmons and E. S. Larsen.

water. When a solution equals about 3.43 per cent sodium chloride at 20° C., the solubility of silver chloride becomes about equal to its solubility in water, and it increases with the concentration of the solution. Such concentration rarely, if ever, exists in weathered

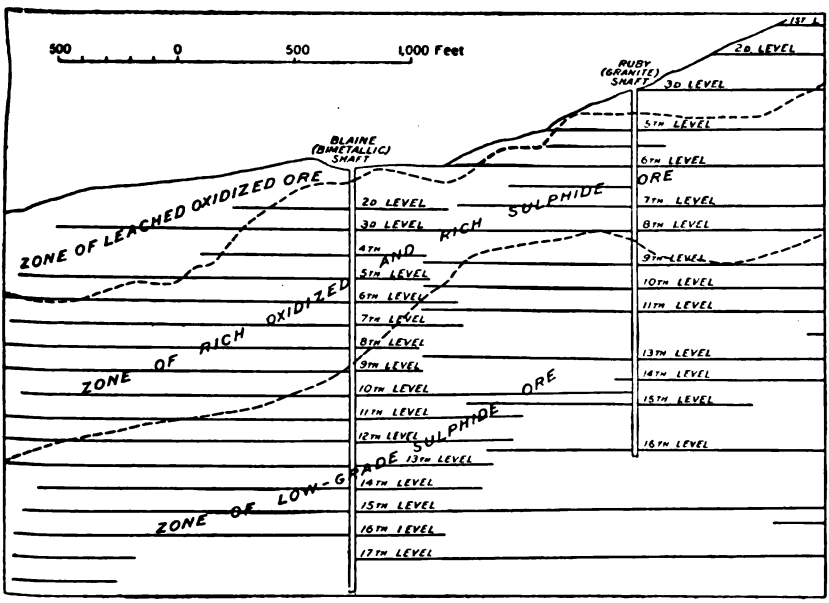

FIGURE 17.—Longitudinal or vertical projection of Granite-Bimetallic vein, Philipsburg, Mont. After W. H. Emmons and F. C. Calkins.

zones of ore deposits. In arid regions, also, smaller amounts of water will percolate through the ores than in wet regions. Many deposits of silver ore in the Great Basin region of North America were enormously rich at their outcrops but proved to be profitless below a depth of 100 feet. Silver chloride forms in moderate

amounts also in countries that are comparatively moist, although, as already stated, it is most abundant in dry countries. Silver-bearing pyromorphite and native silver also are found in outcrops of silver deposits.

It is noteworthy that few silver deposits have been found in districts where the outcrops of the lodes did not at some place carry silver, though it occurs only in relatively small amounts at the outcrops of some lodes. At Philipsburg, Mont., where chlorides of silver are not abundant, the outcrop of the richest lode, although it carried silver, was so poor in silver that the location was allowed to lapse by the first locator. The deposit subsequently produced over $32,000,000 in silver and gold. As a general rule, however, the outcrops of silver deposits will show appreciable silver, and in this respect, the deposits of silver differ from those of copper, whose outcrops at many places are almost completely leached of copper.

SILVER-GOLD DEPOSITS.

The concentration of silver as chloride or native metal at the outcrop and in the superficial zone is at many places attended by a concentration of gold, due doubtless to a decrease in the volume of the ore and gangue minerals by weathering. If the deposits contain manganese, gold may be carried downward and be redeposited below. Thus there may be a zone at and near the surface in which silver is concentrated, whereas gold will become increasingly greater in quantity with increase in depth, as at the Exposed Treasure mine, near Mojave, Cal. At Creede, Colo., in the Amethyst vein, where manganese is abundant and carbonates are rare, silver is most highly concentrated a short distance below the surface. (See fig. 16, p. 267.) Although the chloride in this deposit is not so important as native silver, gold is nevertheless found in greatest concentration below the zone where silver is most abundant. In general, however, gold is more readily precipitated than silver minerals, except the chloride of silver, especially where the gold-silver ore has calcite gangue. Secondary gold may be found below deposits of silver chloride and it may be associated with deposits of silver sulphide, the gold in some places extending to nearly equal depths. Under some conditions secondary gold may form as deep as or deeper than native silver. If there is a zone of complex secondary sulphosalts of silver, secondary gold is generally if not invariably concentrated in the upper rather than in the lower parts of such a zone. (See fig. 17, p. 267.)

SILVER-LEAD DEPOSITS.

A common type of silver ore, particularly in the western part of the United States, is composed of argentiferous galena, pyrite, sphalerite, and other minerals. The zinc is leached out by weather-

ing, leaving the lead and silver in a concentrated form. If the deposits are in limestone the zinc is precipitated extensively as carbonate along fractures and bedding planes, extending outward and particularly downward from the altered lead-silver ore. Some parts of the argentiferous galena ore that lies between fractures will weather slowly, and these will remain in the oxidized zone. Frequently they are surrounded by cerusite, within which there is a shell of anglesite, which in turn incloses the galena. Silver may be concentrated with galena in its outer part. L. D. Ricketts,[1] while investigating the deposits of Leadville, Colo., was, I believe, the first to show this relation, which is a common feature of lead-silver ores in the oxidizing zone. Tolman[2] mentions a galena crystal, the outside of which assayed 100 ounces of silver to the ton, surrounding a core that assayed only 5 to 10 ounces of silver.

According to S. F. Emmons,[3] silver at Leadville during secondary alteration is disseminated through the country rocks adjoining the lead-silver deposits at places where little or no lead is found. He says:

> Silver has been further removed from its original locus and more widely disseminated than lead. In fact it may be assumed that the outlines of the present bodies of lead ore vary but little from those of the original deposits, but it would hardly be safe to make such an assumption in regard to silver ores.

Antimony sulphides, like lead sulphide, alter to stable oxidized compounds. Silver is probably leached from them more rapidly than antimony. (See p. 410.)

SILVER-COPPER DEPOSITS.

Silver and gold may be found in notable concentration at the outcrops of copper deposits that carry little or no copper at the surface, as at Butte, Mont. In general secondary silver minerals and gold are precipitated nearer the surface than secondary copper minerals. Copper may be held in solution as sulphate in the presence of ferrous sulphate, but ferrous salt precipitates silver and gold, so that silver and gold will be thrown out of a solution that is depositing chalcocite. (See p. 157.) Moreover chalcocite itself precipitates gold and silver almost instantly. It follows that in copper deposits no precious metals of secondary origin will be found below an extensive chalcocite zone.[4] At Butte the superficial secondary silver ores

[1] Ricketts, L. D., The ores of Leadville, p. 37, Princeton, 1883.

[2] Tolman, C. F., jr., Secondary sulphide enrichment: Min. and Sci. Press, vol. 106, p. 141, 1913.

[3] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 553, 1886.

[4] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, p. 42, 1912.

graded downward into secondary copper ores. Rich gold ores were found above the copper ores now mined at Mount Morgan, Queensland. At Jerome, Ariz., in the Highland Boy mine, Bingham, Utah, and elsewhere, ores that carry the precious metals near the surface become cupriferous ores farther down.

OCCURRENCE OF SILVER MINERALS.

Native silver is a primary mineral in some deposits, as in the zeolitic copper ores of Lake Superior, but in sulphide deposits it is generally or invariably secondary. In some districts it is among the most important ore minerals. It commonly occurs as thin flakes or as sheets plastered on the older minerals or as veinlets filling cracks in the ore and presumably has been formed at many places through the reduction of silver sulphides or other silver-bearing minerals.

Bastin[1] has observed the intimate association of bornite, chalcocite, and native silver in the Up-to-Date mine near Caribou, Colo. (See fig. 18.)

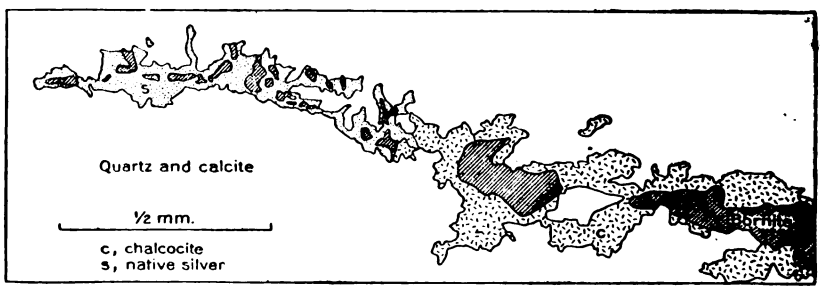

FIGURE 18.—Veinlet showing chalcocite, bornite, and native silver as secondary minerals; replacement veinlet in altered pyroxenite from the Up-to-Date tunnel, Caribou, Colo. After Chase Palmer and E. S. Bastin.

Ferrous sulphate precipitates silver from sulphate solutions, according to the following reaction:

$$Ag_2SO_4+2FeSO_4=2Ag+Fe_2(SO_4)_3.$$

The subject is fully treated by H. C. Cooke,[2] who shows decreasing solubility of silver as ferrous iron increases. This relation doubtless accounts for some well-authenticated occurrences of native silver veinlets below the water level. Tetrahedrite, tennantite, galena, chalcocite, covellite, niccolite, smaltite, chalcopyrite, and many other natural sulphides precipitate the metal from either acid or nearly neutral solutions.[1] In general it is found not more than 1,000 feet

[1] Palmer, Chase, and Bastin, E. S., Metallic minerals as precipitants of silver and gold: Econ. Geology, vol. 8, p. 163, 1913.

[2] Cooke, H. C., The secondary enrichment of silver ores: Jour. Geology, vol. 21, p. 17, 1913.

below the surface and in most of the occurrences within 500 feet of the surface. At Creede, Colo.,[1] some native silver is found 1,100 feet below the surface and perhaps at greater depths but not at depths below 1,200 feet. In that district it forms rich-chalcedonic silver ores and occurs as sheets and wires. In the Aspen mining district, Colorado, native silver coats crystals of barite and is undoubtedly of relatively late deposition. Wire silver piercing barite is found 900 feet below the surface.[2] According to Spurr,[3] silver replaces organic remains in the Aspen district and is found probably 600 feet below the level of ground water. There, he says, in consequence of reduction by carbonaceous matter in the "Weber shales" it has formed instead of the complex salts of silver, which generally constitute the richer ores in this metallogenetic province. By processes of reduction native silver forms as an alteration product of many minerals, such as argentite, pyrargyrite, proustite, polybasite, and stephanite. At many places it is pseudomorphous after these. Vogt[4] says that the native silver of Kongsberg, which is noted for its large and beautiful specimens, is formed by the reduction of argentite. Weed[5] states that secondary silver ore at Butte is probably first precipitated as argentite, which alters to the native metal. Weed notes also[6] its occurrence in mossy aggregates and coatings in fracture planes and cavities of chalcocite in or near the oxidizing zone.

At Philipsburg, Mont.,[7] native silver is an important ore mineral in the silver-gold fissure veins in granite and in the silver-bearing replacement veins in calcareous rocks. It occurs as thin sheets or as flakes, which cut the quartzose ore, and has presumably been formed through the reduction of silver sulphides or of silver-bearing solutions. It is most abundant in the upper part of the enriched zones of the lodes but was encountered as far as 700 feet below the surface. It is not abundant in the San Francisco region, Utah, but was found in oxidized ore near the water level in the Harrington-Hickory mine.[8] At Park City, Utah, also it is comparatively rare.[9] At Leadville, Colo., according to S. F. Emmons,[10]

[1] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede district, Colo.: U. S. Geol. Survey Bull. (in preparation).

[2] Lindgren, Waldemar, oral communication.

[3] Spurr, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, p. 233, 1898; Ore deposition at Aspen, Colo.: Econ. Geology, vol. 4, p. 315, 1909.

[4] Vogt, J. H. L., Ueber die Bildung des gediegenen Silbers, besonders des Kongsberger Silbers, durch Secondärprocesse aus Silberglanz und anderen Silbererzen: Zeitschr. prakt. Geologie, vol. 7, pp. 113–123, 177–181, 1899.

[5] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 102, 1912.

[6] Idem, p. 80.

[7] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 153, 1913.

[8] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[9] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 106, 1913.

[10] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 545, 1886.

native silver is very rare. Considerable amounts of silver were found in upper parts of the Elkhorn mine, Mont.,[1] where it occurred as scales and plates.

In the Comstock lode native silver is rare but has been noted. At Georgetown, Colo.,[2] polybasite is covered with small specks of native silver, which is probably secondary to the polybasite. At Tonopah, Nev., native silver is not abundant but has been observed coating cracks in the primary ore, and is entirely secondary.[3] In the Coeur d'Alene district, Idaho, wire silver is associated with cerusite and limonite in the upper parts of several of the lead-silver veins.[4] It was an important ore in silver veins and in oxidized portions of copper veins at Butte and in several other districts of Montana.

In the Cobalt district, Ontario,[5] much of the native silver occurs in cracks in the earlier deposited minerals—in smaltite, niccolite, and calcite or dolomite. It commonly forms veinlets in the wall rock of the veins, especially in the diabase. Bowlders of granite a foot or more in diameter, occurring in conglomerate, contain delicate veinlets of silver, including some crystals. The mineral is usually found in masses or slabs, flakes, and films, and hair silver is found in vugs. Some of the native silver carries mercury. The native silver at Cobalt appears to represent two or more periods of deposition. The purer, better crystallized, less common variety seems to have been deposited later than the more impure varieties. Miller regards the later silver as an alteration product, but he believes the earlier, less pure variety may be primary. (See p. 303.)

Cerargyrite (horn silver, AgCl) is probably unknown as a primary constituent of ores deposited by ascending hot waters but is commonly developed by weathering, alteration, or enrichment at or near the outcrops of silver-bearing sulphide lodes. A list of its occurrences would include nearly all sulphide deposits in which silver is an important metal. In arid undrained areas it is an important ore mineral, so important that the term "chloriding" is generally used in such regions for pocket hunting near the surface. It is fairly stable at the surface, particularly in arid countries. Prospectors frequently pan the gossan for cerargyrite in prospecting supposed silver veins, and it is found sparingly in sluice boxes at some gold placer mines. At many places, even where the primary

[1] Weed, W. H., Geology and ore deposits of Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 466, 1901.

[2] Spurr, J. E., and Garrey, G. H., Preliminary report on the ore deposits of the Georgetown mining district, Colorado: U. S. Geol. Survey Bull. 260, p. 119, 1905.

[3] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 95, 1905.

[4] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 90, 1908.

[5] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, p. 13, 1913.

sulphide ores are not profitable, the superficial chloride ores may be very rich. At the Silver Cliff quarry, Custer County, Colo.,[1] an area several hundred feet in diameter in shattered iron-stained rhyolite carried silver as cerargyrite to depths of 30 or 50 feet. The rhyolite near the surface carried some 35 to 50 ounces of silver to the ton, but that which lay deeper carried less than 7 ounces.

The chloride ores generally pass into the sulphides below, and the bottom of the zone of ore carrying horn silver is generally above the bottom of the zone of secondary silver sulphides. Cerargyrite is not everywhere confined to the shallow-surface zone, however. In the Comstock lode, where it is not particularly abundant, it was noted, according to Clarence King, at a depth of 900 feet below the surface. In the Horn Silver mine, Utah, silver chloride was found by Butler[2] in oxidized ores on the seventh level.

In the Evening Star mine, Leadville, Colo.,[3] a considerable body of cerargyrite was found in highly decomposed porphyry, stained with iron oxide along the joints. Unlike the ores in limestone, this ore was practically free from lead.

Cerargyrite forms where waters carrying silver sulphate or carbonate encounter waters bearing chlorides. Silver chloride is only slightly soluble in ordinary ground water and is therefore fairly stable under surface conditions. Many deposits of cerargyrite ores contain large amounts of manganese oxide. In some of these native silver is present only in small quantity. The presence of manganese oxide delays the generation of ferrous sulphate, which, as already stated, precipitates native silver from ferric sulphate solution. With manganese dioxide in the presence of abundant chlorides horn silver would be precipitated rather than the native metal. Examples of horn-silver ores associated with manganese oxides include the famous deposits of Lake Valley,[4] near Silver City, N. Mex., the deposits of the Exposed Treasure mine,[5] near Mohave, Cal., and some silver deposits at Neihart, Mont.,[6] and at Leadville, Colo.[7] Other deposits, however, containing appreciable though lower proportions of man-

[1] Emmons, S. F., Mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 450, 1896.

[2] Butler, B. S., op. cit., p. 96.

[3] Ricketts, L. D., op. cit., p. 38.

[4] Clark, Ellis, The silver mines of Lake Valley, New Mexico: Am. Inst. Min. Eng. Trans., vol. 24, p. 148, 1895. Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 66, 279, 1910.

[5] De Kalb, Courtenay, Geology of the Exposed Treasure lode, Mojave, Cal.: Am. Inst. Min. Eng. Trans., vol. 38, p. 319, 1908.

[6] Weed, W. H., Geology of the Little Belt Mountains, Montana, with notes on the mineral deposits of the Neihart, Barker, Yogo, and other districts, accompanied by a report on the petrography of the igneous rocks of the district by L. V. Pirsson: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 407, 1900.

[7] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 562, 1886.

ganese, contain considerable native silver with subordinate chloride; a conspicuous example is the Amethyst vein of Creede, Colo.

The effect of manganese dioxide in silver deposits in the presence of chloride offers attractive problems for chemical investigation.

Embolite and bromyrite.—Embolite, Ag(Cl,Br); bromyrite, AgBr; iodobromite, Ag(Cl, Br, I); and iodyrite, AgI, are not common minerals, for they contain bromine and iodine, which are rare in mineral solutions. None of them are known to have been formed in hot ascending solutions. They are in the main even less soluble in water than cerargyrite and are therefore comparatively stable when once they are formed.

The term "silver bromides" is very popular in certain parts of the West and is frequently applied to green earthy material that carries silver. I have examined such material in Montana, Colorado, and Nevada and have found that examined to be either pyromorphite, copper carbonate, or chrysocolla, some of it with silver in an undetermined state, but probably as the chloride and native metal. The mutual relations of the silver halides at Tonopah, Nev., have already been reviewed (p. 257).

Iodyrite, AgI, is a rare mineral found exclusively in the secondary zones of silver deposits. Iodine is so rare an element that its concentration in silver deposits is noteworthy and presents another example of the tendency of the elements to segregate during oxidation. In the Broken Hill district,[1] New South Wales, crystals of iodyrite are associated with limonite and psilomelane. At Tonopah[2] iodyrite of secondary origin is found in crystalline crusts on quartz. Iodyrite is also found at Lake Valley, N. Mex., and at several places in Mexico.

Argentite, Ag_2S, is one of the commonest and most valuable secondary silver minerals, but it occurs also as a primary mineral. It fills postmineral cracks in the secondary zones at Georgetown, Colo., Neihart and Philipsburg, Mont., and many other places. Great bonanzas of argentite were found in upper levels on the Comstock lode. In this lode it has been identified as far as 3,000 feet below the surface but not certainly as a secondary mineral. At Tonopah, Nev.,[3] some occurrences of argentite are primary, but in places it coats crevices that cut the primary ore and is evidently secondary also. Some of the ores show argentite fringing cerargyrite as if secondary to it. It is probably primary in part at Butte, Mont., and at Tintic, Utah. Argentite is pseudomorphous after ruby silver (and vice versa) at Joachimsthal, Bohemia. At Cobalt,

[1] Kraus, E. H., and Cook, C. W., Iodyrite from Tonopah, Nev., and Broken Hill, New South Wales: Am. Jour. Sci., 4th ser., vol. 27, p. 212, 1909.

[2] Idem, p. 213.

[3] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, pp. 92, 94, 1905.

Ontario,[1] it is common but less abundant than native silver. In this district well-developed crystals, as well as the massive variety, are found.

Silver sulphide is the least soluble sulphide of the commoner metals, except those of mercury and bismuth, and in reactions involving double decomposition it would be precipitated from argentiferous solutions before all except those sulphides. A search for pseudomorphs after copper sulphides, sphalerite, and pyrite has shown surprisingly few clearly defined examples, although it probably does replace these sulphides metasomatically. If sulphuric acid should in its descent encounter a soluble sulphide like zinc blende, hydrogen sulphide and zinc sulphate might be formed. The hydrogen sulphide would precipitate silver sulphide from a solution containing Ag_2SO_4.

The precipitation of argentite from silver sulphate solution does not necessitate a change in valence like that which takes place when chalcocite is formed. Argentite could be precipitated in any of the following reactions:

$$H_2S+Ag_2SO_4=H_2SO_4+Ag_2S.$$
$$ZnS+Ag_2SO_4=ZnSO_4+Ag_2S.$$
$$PbS+Ag_2SO_4=PbSO_4+Ag_2S.$$

The concentration of silver in weathering galena is discussed on page 57.

Pyrargyrite, dark ruby silver, $3Ag_2S.Sb_2S_3$, is probably the most valuable secondary silver mineral in a large number of silver mines in the United States. So far as known, it is confined to epigenetic deposits, and it is particularly conspicuous in many deposits of early and middle Tertiary age in the American Cordillera. It is not known as a primary mineral of contact-metamorphic and nearly related deposits. In the Granite-Bimetallic mine, at Philipsburg, Mont., pyrargyrite is perhaps the most important mineral.[2] It occurs as small specks intimately intergrown with quartz and stibnite that may possibly be primary, but it is very much more abundant as a secondary mineral in this mine. Crystals as large as cherries line vugs, but most of it occurs in small veinlets that cut across the banding of the primary ore, in which stibnite is abundant. At Tonopah, Nev., pyrargyrite coats crevices that cut the primary ore and is evidently secondary.[3]

The assumption that pyrargyrite forms under conditions of sulphide enrichment rests mainly on paragenetic evidence and the fact that it commonly disappears with increase in depth. Pyrargyrite

[1] Miller, W. G., op. cit., p. 20.

[2] Emmons, W. H., and Calkins, F. C., op. cit., p. 154.

[3] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 94, 1905.

is an important ore mineral at Georgetown, Lake City, Ouray, and Telluride, Colo.; at the Comstock lode, Austin, Tuscarora, and other districts of Nevada; and at Neihart, Butte, and other places in Montana. At all these places it is probably, in part, at least, of secondary origin.

Pyrargyrite is an important constituent of the ore of the famous silver mines of Zacatecas, Guanajuato, and Pachuca, Mexico. Mineralogically the ores of these deposits are nearly related to those of the Comstock lode and Tonopah, Nev.

On the horizon of pyrargyrite at Lake City, Colo., the following, from Irving and Bancroft,[1] is a particularly clear statement:

> Ruby silver occurred, so far as could be learned, in all of the mines at the plane of demarcation between sulphides and oxides and, in generally decreasing quantity, to several hundred feet below this level. Along cracks and fissures it occurred in isolated masses to great depths—for instance, at 1,200 feet in the Golden Fleece and at 1,300 feet in the Ilma. These deep occurrences are, however, uncommon and merely indicate the presence of some easy line of access for downward-moving solutions.
>
> Ruby silver has probably resulted from the solutions of silver and antimony obtained by the decomposition of the tetrahedrite and possibly to some extent also from the argentiferous galena. The chemistry of both the solution and reprecipitation of the antimonial and arsenical sulphur compounds has not yet been worked out in sufficient detail to permit a statement of the probable steps of the process, but the geological facts show that it has occurred. The proofs of the secondary character of the ruby silver are:
>
> 1. Its restriction in quantity to the upper levels of the mines.
> 2. Its invariable occurrence as the latest deposited mineral in the veins, either in cracks or crevices in shattered primary ore or as crystals in cavities.
> 3. Its occurrence only in isolated bunches in deeper workings, where its origin is probably due to the presence of water channels that permit the downward percolation of water from above.
> 4. Its complete absence from the great mass of deep-seated ore.

In some mines ruby silver is found at very considerable depths, however, possibly below the zone of secondary alteration. At Przibram, for example, it is said to be found 3,500 feet below the surface. Pyrargyrite, like stephanite, probably forms in alkaline solutions. (See p. 262.)

Proustite, light ruby silver, $3Ag_2S.As_2S_3$, is similar to pyrargyrite in its occurrence and is commonly regarded as a secondary mineral. Whether it is ever primary is a moot question. Proustite is a secondary mineral at Lawson, Lake City, Ouray, Silverton, Telluride, and Rico, Colo., at Philipsburg, Mont., at Austin, Nev., Neihart, Mont., in the Coeur d'Alene district, Idaho,[2] and in several other districts. It has been noted on the Comstock lode but is not abun-

[1] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, pp. 63, 97, 1911.

[2] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 93, 1908.

dant there. A little is found in Cobalt veins, particularly in those in the diabase.[1]

Discussing the genesis of argentite, proustite, pyrargyrite, stephanite, and polybasite, Ransome[2] says:

> It is quite possible that further study of ore deposits may result in showing that some of these minerals, especially proustite, are fully as characteristic of downward enrichment as is chalcocite.

Sommerlad[3] prepared proustite by heating silver chloride and arsenic trisulphide, and many other syntheses are known.[4] I have no record of the formation of proustite in cold sulphate waters.

Stephanite, brittle silver, $5Ag_2S.Sb_2S_3$, is an important mineral in the Comstock lode, at Tuscarora and Tonopah, Nev., at Georgetown, Lawson, Aspen, and Rico, Colo., and in many other silver districts. It generally accompanies ruby silver and polybasite, and in some districts it occurs, like them, in cracks cutting the primary ore.[5] In the Comstock lode, according to King,[6] broken fragments of quartz themselves containing ore have been recemented by sheets of stephanite. In general, its occurrences in the United States are not clearly described, and its genesis is more or less uncertain.

According to Fenner,[7] stephanite replaces feldspar in ores of Leadville, Colo. On the synthesis of stephanite see experiments of Grout (p. 262) and Ravicz (p. 263).

Polybasite, $9Ag_2S.Sb_2S_3$, is commonly a secondary mineral. It occurs at Georgetown and Lawson, Colo., in cracks cutting the primary ore,[8] and in the main is related to the present surface. At Neihart, Mont.,[9] it occurs in postmineral fractures and in vugs and incrusts primary sulphides. At Neihart it is found also replacing galena along its cleavage cracks.[5] It occurs with barite in the Mollie

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[1] Miller, W. G., op. cit., p. 24.

[2] Ransome, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 211, 1910.

[3] Sommerlad, Hermann, Über einige Versuche zur Herstellung von Sulfantimoniten und Sulfarseniten des Silbers auf trockenem Wege: Zeitschr. anorg. Chemie, vol. 15, 1897, p. 177; Über Versuche zur Darstellung von Sulfantimoniten und Sulfarseniten des Silbers, Kupfers und Bleis auf trockenem Wege: Idem, vol. 18, pp. 420–447, 1898.

[4] Clarke, F. W., The data of geochemistry, 3d. ed.: U. S. Geol. Survey Bull. 616, p. 654, 1916.

[5] Bastin, E. S., Metasomatism in downward sulphide enrichment: Econ. Geology, vol. 8, p. 61, 1913.

[6] King, Clarence, The Comstock lode: U. S. Geol. Expl. 40th Par., vol. 3, p. 81, 1870.

[7] Fenner, C. N., A replacement of rhyolite porphyry by stephanite and chalcopyrite at Leadville: School of Mines Quart., vol. 31, p. 235, 1910.

[8] Spurr, J. E., and Garrey, G. H., Economic geology of the Georgetown quadrangle (together with the Empire district), Colo., with general geology by S. H. Ball: U. S. Geol. Survey Prof. Paper 63, p. 261, 1908.

[9] Weed, W. H., Geology of the Little Belt Mountains, Mont., with notes on the mineral deposits of the Neihart, Barker, Yogo, and other districts, accompanied by a report on the petrography of the igneous rocks of the district by L. V. Pirsson: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 407, 1900.

Gibson mine at Aspen, Colo., where it alters to native silver.[1] It is probably secondary in the Comstock lode, Nevada, and in several districts in San Juan, Colo. At Tonopah, Nev.,[2] polybasite is found as deep as 500 feet below the surface in fractures that cut older sulphides, but, according to Spurr, it is not certain that it was deposited by descending solutions. In many other districts it is regarded as a secondary mineral, for it is not abundant in the deeper levels.

Although polybasite has been formed synthetically, no record of its synthesis from cold sulphate waters is available. H. C. Cooke[3] treated powdered stibnite with cold dilute silver sulphate solution and obtained a rich antimony-silver ore but did not identify the material as polybasite. (See p. 263.)

Pearceite, $9Ag_2S.As_2S_3$, is less common than the corresponding antimony salt, polybasite. It is generally assumed to be secondary. According to Weed,[4] it constitutes much of the rich silver ore of Neihart, Mont. Pearceite, intimately associated with galena, has been identified[5] from the Mollie Gibson mine, Aspen, Colo. In the Drumlummon mine, Marysville, Mont., according to Penfield,[6] it lines a vug and is intimately associated with chalcopyrite, calcite, and quartz.

Tetrahedrite, gray copper, $4Cu_2S.Sb_2S_3$, is rather widely distributed but is of subordinate importance as a source of copper. The argentiferous variety, freibergite, is a valuable source of silver in many deposits. In the San Juan region, Colorado, tetrahedrite is abundant in many deposits and is regarded as a primary constituent in this region.[7] It is primary at Butte, but its corresponding arsenic compound, tennantite, is said to be secondary.[8] In the Leonard mine some tetrahedrite is later than enargite.[9] At Ouray and Lake City, Colo., according to Irving and Bancroft,[10] it was deposited by ascending hot waters but mainly in the upper parts of the lodes, which at Lake City have a vertical range of over 5,000 feet. The corresponding arsenic compound, tennantite, has not been recognized.

[1] Spurr, J. E., Geology of the Aspen mining district, Colorado, with atlas: U. S. Geol. Survey Mon. 31, pp. 224–225, 1898.

[2] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 95, 1905.

[3] Unpublished data.

[4] Weed, W. H., The enrichment of gold and silver veins, in Pošepný, Franz, The genesis of ore deposits, p. 494, 1902.

[5] Penfield, S. L., On pearceite, a sulpharsenite of silver, and on the crystallization of polybasite: Colorado Sci. Soc. Proc., vol. 5, p. 211, 1896.

[6] Idem, pp. 217–218.

[7] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: U. S. Geol. Survey Bull. 182, p. 78, 1901; Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 212, 1910.

[8] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[9] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 78, 1912.

[10] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, pp. 34, 52, 1911.

Tetrahedrite appears to be primary in Clear Creek County, Colo.[1] At Cripple Creek, Colo., it is primary and persists to depths of 2,000 feet below the surface.[2] It is found also at Nevada City[3] and, intergrown with electrum, at Ophir, Cal.[4] At Elkhorn, Mont.,[5] it is abundant and is rich in silver. According to Weed, it is probably the parent sulphide of rich altered silver ores. A little is present at Cobalt, Ontario.[6]

At Bingham, Utah, according to Boutwell,[7] tetrahedrite is secondary. Crystals of pyrite are coated by chalcopyrite and the latter by tetrahedrite. In the Centennial mine,[8] in the Empire district, Colorado, tetrahedrite forms in cracks of chalcopyrite in auriferous lodes and is said to be derived from it. Tetrahedrite is associated with the later ores of the Cactus mine,[9] San Francisco district, Utah. It is said to be secondary at Rio Tinto,[10] Spain.

At Park City, Utah, beautiful crystals of tetrahedrite line vugs[11] in chalcopyrite. In the Kirwin district, Wyoming,[12] tetrahedrite, with galena, is developed after chalcopyrite. Secondary argentiferous tetrahedrite appears to have formed on an extensive scale in the Caledonia mine,[13] Idaho, where it fills cracks and coats chalcopyrite.

Tetrahedrite occurs abundantly in the Mount Lyell mine, Tasmania, according to Gilbert and Pogue.[14] With some chalcopyrite it occurs as replacement rims on bornite grains and is distinctly later than bornite. The interesting occurrences of primary tetrahedrite veinlets which cut older sulphides in the Mina Mexico vein, Sonora,[15] are mentioned on page 78.

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[1] Kemp, J. F., Secondary enrichment in ore deposits of copper: Econ. Geology, vol. 1, p. 22, 1906.

[2] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 121–122, 1906.

[3] Lindgren, Waldemar, The gold-quarts veins of Nevada City and Grass Valley districts, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 119, 1896.

[4] Lindgren, Waldemar, The gold-silver veins of Ophir, Cal.: U. S. Geol. Survey Fourteenth Ann. Rept., pt. 2, p. 273, 1894.

[5] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 450, 1901.

[6] Miller, W. G., op. cit., p. 26.

[7] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, pp. 107, 220, 222–223, 1905.

[8] Spurr, J. E., and Garrey, G. H., Economic geology of the Georgetown quadrangle (together with the Empire district), Colorado, with general geology by S. H. Ball: U. S. Geol. Survey Prof. Paper 63, p. 148, 1908.

[9] Butler, B. S., op. cit., p. 96.

[10] Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, p. 411, 1910.

[11] Specimen in Geological Museum of University of Minnesota.

[12] Hewett, D. F., The ore deposits of Kirwin, Wyo.: U. S. Geol. Survey Bull. 540, p. 130, 1914.

[13] Shannon, E. V., Secondary enrichment in the Caledonia mine, Coeur d'Alene district, Idaho: Econ. Geology, vol. 8, p. 569, 1913.

[14] Gilbert, C. G., and Pogue, J. E., The Mount Lyell copper district of Tasmania: U. S. Nat. Mus. Proc., vol. 45, p. 609, 1913.

[15] Hynes, D. P., Notes on the geology of the Mina Mexico vein: Econ. Geology, vol. 7, p. 285, 1912.

Tetrahedrite has not been formed synthetically under conditions that prevail in the secondary sulphide zone. The formula of the argentiferous variety, freibergite, has been written as a combination of chalcocite, argentite, and stibnite—$4(Cu_2S.Ag_2S)Sb_2S_3$—but as these minerals have dark streaks and freibergite has a reddish-brown streak, this interpretation of the formula is open to question. Possibly the molecule of ruby silver (red streak) is present. That tetrahedrite may be formed by alteration near the surface is suggested by several occurrences noted above and by its occurrence on Roman bronze coins at hot springs[1] at Bourbonne.

Tennantite, $4Cu_2S.As_2S_3$, is regarded as having the same range of occurrence as the corresponding antimony sulphide, tetrahedrite. It is not so common, however, and comparatively few detailed descriptions of its occurrence as a secondary mineral are available. It is said to be secondary at Butte, Mont.,[2] where, according to Emmons and Tower, it seems to result from the decomposition of enargite, with which it is always associated.

Other silver minerals.—Several other silver minerals, all comparatively rare species, have been regarded as secondary. Among these are stromeyerite,[3] $(Ag, Cu)_2S$; dyscrasite,[4] $Ag_6Sb(?)$; and possibly stetefeldtite.[5] Of these, stromeyerite corresponds in composition to some argentiferous chalcocite. In the Yankee Girl mine, near Silverton, Colo., it is associated with chalcocite and bornite. Since secondary sulphides of silver and copper are precipitated together, it would be supposed that stromeyerite would develop in many deposits. The silver compound in argentiferous chalcocite has not yet been identified, however. Dyscrasite is an important ore mineral at Cobalt, Ontario.

SILVER-BEARING DEPOSITS.

LEADVILLE, COLORADO.

Leadville, Colo.,[6] is in an area of Paleozoic limestones, quartzites, and shales that are intruded by dikes and sills of acidic porphyries. Normal faulting has taken place on an extensive scale. The climate is moist, the altitude high. The most important deposits are found

[1] Daubrée, A., Compt. Rend., vol. 80, p. 461, 1875.

[2] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte special folio (No. 38), p. 6, 1897.

[3] Emmons, S. F., The secondary enrichment of ore deposits: Am. Inst. Min. Eng. Trans., vol. 30, p. 196, 1901.

[4] Smith, George, The ore deposits of the Australian Broken Hill Consols mine, Broken Hill, New South Wales: Am. Inst. Min. Eng. Trans., vol. 26, pp. 69–78, 1897.

[5] Spurr, J. E., Ore deposits of the Silver Peak quadrangle, Nevada: U. S. Geol. Survey Prof. Paper 55, p. 120, 1906.

[6] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, 1886. Emmons, S. F., and Irving, J. D., The Downtown district of Leadville, Colo.: U. S. Geol. Survey Bull. 320, 1907. Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, pp. 282–288, 1911.

in Carboniferous limestone at or near its contact with an overlying porphyry, which is generally the "White porphyry." Thus the ores constitute a sort of sheet, the upper surface of which, being formed by the base of the porphyry sheet, is comparatively regular, while the lower surface is ill defined and irregular, there being a gradual transition from ore to limestone, the ore extending to varying depths below the surface, occupying in places the entire thickness of the Leadville ("Blue") limestone. Other deposits include, however, steeply dipping veins, some of them in fault fissures, and irregular masses or sheets in limestone near the "Gray" or other porphyries.

The ore that is most abundant and that is economically by far the most important is argentiferous galena and its secondary products, cerusite, or carbonate of lead, and cerargyrite, or chloride of silver. Lead is also found as anglesite and pyromorphite and occasionally as oxide in the form of litharge or, more rarely, of minium. Silver occurs commonly as chloroiodide and is very rare in the native state. The gangue minerals include quartz, chert, barite, siderite, and clay, the clay being commonly charged with iron and manganese oxides or with sulphates.

A common alteration product of mixed pyrite and galena, a product that is associated in considerable quantity with the ore bodies, is "basic ferric sulphate," an ocherous substance of somewhat uniform appearance but of varying composition, mainly a mixture of jarosite, or yellow vitriol, and hydrated basic ferric sulphate, with more or less anglesite and pyromorphite. Manganiferous siderite on oxidation yields manganese oxides.

Gold occurs in the native state, generally in extremely small flakes or leaflets. It is also said to have been found in the filiform state in galena. Other minerals are zinc blende, calamine, arsenic (probably as sulphide), antimony (probably as sulphide), wulfenite, copper carbonate and silicate, and bismuth sulphide.

In depth the ores consist of pyrite, sphalerite, and galena in fairly equal amounts, with some chalcopyrite and other minerals.

Nodules of galena surrounded by lead carbonates are locally numerous in the oxidized zone. Several of these nodules have been assayed, and the sulphide has been found to carry about six times as much silver as the surrounding carbonate shell.[1]

Emmons[2] states that gold exists in the limestone ores only in traces. In certain veins of sulphide ores below the porphyry contacts, according to G. Montague Butler,[3] some small masses of sphaleritic manganiferous ores are very rich in gold. A picked

[1] Ricketts, L. D., The ores of Leadville, p. 37, Princeton, 1883.

[2] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 545, 1886.

[3] Butler, G. M., Some recent developments at Leadville: Econ. Geology, vol. 7, p. 318, 1912.

sample assayed 8 ounces per ton. Silver is found in the oxidized ores mainly as chloride. It is a generalization of the miners of the region, according to Emmons,[1] that rich silver chloride ores are likely to accompany manganese. As suggested by him and as mentioned on a previous page of this paper (p. 273), it is possible that the agency of manganese in the generation of free chlorine is important in connection with the precipitation of silver chloride under some conditions.

In general, silver diminishes in quantity with depth. The upper contact bodies as a whole were richest in silver; the "second contact" bodies were slightly lower in tenor; and at lower horizons the ore is of distinctly low grade.[2]

Very recently large bodies of iron-stained smithsonite and of monheimite (see p. 387) have been found in the oxidized zones below lead-carbonate ores. Some of these were formerly supposed to be iron-stained limestone. A. A. Blow[3] maintained that sphalerite is deposited by downward-moving waters just in advance of oxidation, and in this S. F. Emmons[4] appears to concur. Some small veinlets of galena are found also in sulphide ore just below the oxidized zone.

Of considerable interest are some small fractures in the quartzite at a lower horizon, which, as Mr. Emmons informed me, very commonly carry small amounts of high-grade manganiferous gold ore. This ore he regarded as a deposit from descending waters.

ASPEN, COLORADO.

The Aspen district, Colorado,[5] is an area of granite overlain by Paleozoic limestones, sandstones, and shales, which are intruded by dikes and sills of diorite porphyry and quartz porphyry. Structurally the district is a fault mosaic of folded beds, and the principal ore deposits are replacements of limestones in and along fault fissures. The primary ore deposition was effected by ascending magmatic waters and took place in a relatively brief period; but, according to Spurr,[6] it had three successive stages—(1) barite veins, (2) silver sulphides, sulphantimonites, and sulpharsenites, (3) galena and zinc blende—each stage being preceded by slight fracturing of the rocks. The maximum deposition was below shale beds.

Near the surface the ores occur as oxides, sulphates, and carbonates, mixed with sulphides, from which they are evidently

[1] Emmons, S. F., op. cit., p. 562.

[2] Emmons, S. F., and Irving, J. D., op. cit., p. 34.

[3] Blow, A. A., The geology and ore deposits of Iron Hill, Leadville, Colo.: Am. Inst. Min. Eng. Trans., vol. 18, p. 172, 1890.

[4] Emmons, S. F., The secondary enrichment of ore deposits, in Pošepný, Franz, The genesis of ore deposits, p. 440, 1902.

[5] Spurr, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, 1898.

[6] Spurr, J. E., Ore deposition at Aspen, Colo.: Econ. Geology, vol. 4, p. 303, 1909.

derived. The principal ore in these upper zones consists of earthy carbonates and sulphates, chiefly of lead (cerusite and anglesite). Among the oxides hematite and limonite are very common, and the red oxides of copper and lead (cuprite and minium) occur in blotches in the oxidized ores, usually indicating the presence of silver. With increase in distance from the surface the oxides, sulphates, and carbonates disappear and give place to pure sulphides. Argentiferous galena and blende are abundant in the deeper ore, and other sulphides are of less common occurrence. Pyrite and chalcopyrite, with occasional bornite, are also found. Tetrahedrite and tennantite are common and contain a large proportion of silver sulphide. The gangue is quartz and barite.

In the Mollie Gibson and Smuggler mines there is much polybasite, which generally occurs in flesh-colored barite, whose color is due to a small amount of iron oxide. Along watercourses the polybasite is reduced to native silver, so that the ore consists of barite bound together by irregular wires and masses of silver. As this process is attended by some loss of bulk, the ore also becomes much jointed and loses cohesion.

Spurr states that native silver is abundant to depths of at least 900 feet in deposits where the water level stood about 300 feet. Generally the native silver is found near silver sulphides and in fractures that are later than primary mineralization. Nearly all the larger bodies of native silver are on the side of the vein which is formed by shale, and some of them are wholly within the shale wall.

PARK CITY, UTAH.

Park City[1] is in the Wasatch Range, about 25 miles southeast of Salt Lake City. The sedimentary rocks of the district are of Pennsylvanian, Permian (?), Triassic, possibly Jurassic, and Eocene age, and consist of quartzite, limestones, shales, and sandstones. The Eocene rocks grade upward into andesite tuffs and are overlain by andesites. The sedimentary rocks show no discordance in bedding. They are intruded by dikes, sills, stocks, and laccolithic masses of quartz diorite and quartz diorite porphyry. The andesite carries fragments of porphyry and is therefore younger than the porphyry. The andesite grades downward into Eocene rocks. Boutwell concludes, for these reasons, that quartz diorite and quartz diorite porphyry are as late as Triassic and probably older than the Eocene rocks on which the andesite rests.

The intrusion of igneous rocks was attended by the development of zones of garnet in limestone around the igneous bodies, and in

[1] Boutwell, J. M., The geology and ore deposits of the Park City district, Utah, with contributions by L. H. Woolsey: U. S. Geol. Survey Prof. Paper 77, 1912.

some of these zones there are chalcopyrite, sphalerite, and other ores. The principal ore bodies are, however, not garnetiferous. The dominating structure is a great anticline, broken by many faults. Although normal faults probably predominate, there are many reverse faults. As the faults involve the igneous rocks, they were formed, in part at least, after the period of intrusion.

The ore deposits are replacement veins in limestone, quartzite, and porphyry. Although the limestones are interstratified with extensive beds of shale, the shale is not mineralized. The lode deposits are extensive, strong, and valuable. They lie in a few continuous master zones rather than in many small fissures. Examples are the Ontario and Daly West fissure zones and the Silver King and Kearns-Keith fissure zones. The prevailing strike of these fissures is east.

The metallization shows close genetic relation to the intruding rock. The earliest deposits were formed as large tabular bodies parallel to the beds. Later the great cross-cutting fissure zones were formed and metallized. Some of these cut across the earlier deposits and at many places ore shoots of contemporaneous age make out from them parallel to the beds. Thus there are bedding plane deposits of two periods of metallization, but all the deposits are believed to be genetically related to intruded rocks, for they are not found more than a few hundred feet from the intrusives.

The ore minerals are galena, pyrite, chalcopyrite, sphalerite, tetrahedrite, and the usual oxidation products. The gangue minerals are quartz, jasper, fluorite, calcite, and rhodochrosite. Barite is practically unknown in the deposits, the sulphates being represented only by alteration products. Where porphyry lies along the walls it is sericitized, and pyrite and silica were added. The bedded ores are generally richer than the lode ores.

The ores cropped out inconspicuously, and only here and there. Ground water was struck at a depth of 66 feet in Ontario ground, and generally it is high. As in most rugged countries of moist climate, the top of the ground-water level shows great difference in elevation. Even at a depth of 2,000 feet enormous quantities of water were encountered, and a deep adit, after having been completed 10 years, still yielded from 6,000 to 9,000 gallons a minute, the quantity varying with the seasons. This adit drains most of the district.

The oxidation of the deposits reaches a maximum depth of 1,700 feet and averages 600 or 700. It is deeper in the zones of cross fracture than in the bedding-plane deposits. Some of the oxidized ores were obviously submerged. Oxidation, however, is generally incomplete, and galena was found at the outcrop of the Ontario lode.

Although the pyrite is slightly cupriferous, copper first becomes significant with appearance of tetrahedrite. This mineral is believed to be primary and to be contemporaneous with the intergrown galena. Chalcocite is only sparingly present. Silver occurs in galena, pyrite, and sphalerite. It was not found as sulphide nor as oxidation products. There is doubtless some enrichment of silver, however, and in the Ontario lode the richer oxidized ore is said to have been between the 600 and 700 foot levels. Carbonate ores extended below these levels, decreasing in value and amount with increase of depth. On oxidation the manganiferous minerals yield pyrolusite or manganous oxides. According to Boutwell, these oxides are commonly regarded as indications of good ore. The gold ore was richest where the ore was most altered and decomposed, and where manganese was most abundant.[1]

TINTIC DISTRICT, UTAH.

The Tintic district[2] is in central Utah, in a mountainous area that rises some 8,000 feet above the sea and nearly 4,000 feet above the plains. The temperature is moderate, the climate is dry, and most of the streams that drain the area disappear in the loose material of the desert. The area is occupied by a thick series of Paleozoic quartzites, slates, limestones, and sandstones, which are overlain by Tertiary rhyolite and andesite and intruded by monzonite and basalt. The andesite flows are intruded by great masses of monzonite and by basalt dikes, and an andesite equivalent to the monzonite caps the rhyolite.[3] These rocks are folded and extensively fractured and faulted. The late history of the region may be briefly stated as follows:[4]

1. Elevation of the region, with folding of the Paleozoic sedimentary rocks.

2. Erosion, which began with the Mesozoic uplift and continued into the Tertiary, producing a surface with greater relief than that of to-day.

3. Tertiary volcanic activity, the earlier rhyolitic lava filling deep canyons, on the slopes of which talus was cemented by the lava and the later andesite lava flows, largely rejuvenating the deeply eroded mountain range.

4. Fissuring and ore deposition in the more compact igneous and sedimentary rocks.

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[1] Boutwell, J. M., op. cit., p. 103.

[2] Tower, G. W., jr., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, pp. 603–767, 1899.

[3] Idem, p. 657.

[4] Smith, G. O., written communication.

5. Erosion, by which great masses of igneous rock have been removed, with only slight changes in the topography of the limestone ridges, which had been buried in the lavas.

The ore deposits are (1) large fractured zones in sedimentary rocks, chiefly in the limestone; (2) fissure veins in igneous rocks; and (3) contact-metamorphic deposits in sedimentary rocks near intrusive igneous rocks, mainly in the limestone near monzonite.[1]

The metals, named in the order of their importance up to 1898, are silver, lead, gold, and copper. With increasing depth silver and lead have decreased relatively and copper has become more abundant, especially in the Centennial Eureka mine. In 1909 the yield of copper was 6,000,000 pounds, the district ranking in copper production the thirteenth in the United States.

A remarkable feature of the district is the great depth at which the oxidized ores are found. They are deeper, indeed, than the submerged oxidized ore at Bisbee, Ariz., where the deep secondary zone is related to a pre-Comanche erosion surface rather than to the present one. At Tintic, moreover, the ores are probably early Miocene.[2] Since they were formed, however, great masses of igneous rocks, according to Smith,[3] have been removed by erosion.

The deposits of Tintic and the paragenesis of their minerals have recently been described by Lindgren.[4] He recognizes zones of deposition both horizontal and vertical.

1. In the veins in monzonite quartz occurs in well-developed crystals with much pyrite and some galena, enargite, zinc blende, and chalcopyrite.

2. In the sedimentary rocks up to a distance of 1 to 1½ miles north of the contact with the monzonite the gangue is fine-grained replacement quartz, occasionally small druses of well-crystallized quartz, and much barite. The ores contain much enargite, with a little pyrite, tetrahedrite, and famatinite. There are a few shoots of lead ore and the shoots of copper ore contain a little lead. The ores carry also gold and about 20 ounces of silver per ton.

3. Farther north in the same vein zones the deposits in the sedimentary rocks contain principally galena, with a little zinc blende and pyrite. The silver content is higher than farther south, the average of the ores being perhaps 30 to 40 ounces per ton. There

[1] Tower, G. W., jr., and Smith, G. O., op. cit., p. 722.

[2] Smith, G. O., written communication.

[3] Smith, G. O., The mineral crest, or the hydrostatic level attained by the ore-depositing solutions in certain mining districts of the Great Salt Lake basin (discussion of W. P. Jenney's paper): Am. Inst. Min. Eng. Trans., vol. 33, pp. 1060–1062, 1903.

[4] Lindgren, Waldemar, Processes of mineralization and enrichment in the Tintic mining district: Econ. Geology, vol. 10, pp. 225–240, 1915.

is practically no gold. The gangue minerals consist of an extremely fine-grained cherty replacement of limestone or dolomite and barite. This zone continues, as far as known, from 1 or 1½ miles north of the end of the copper zone.

4. Farther north and east, beyond the lead-silver shoots, the mineralization becomes more feeble. The gangue minerals consist of calcite, dolomite, and a little quartz; the ore minerals comprise galena and zinc blende, with a few ounces of silver to the ton.

Gold and copper thus occur on the whole near the monzonite, lead and silver mainly farther away. This arrangement, according to Lindgren, may correspond to deposition in successively cooler zones and a gradual spreading of the ore-forming solutions toward the north until they become so mingled with surface waters that their solvent power declined.

The variation in ore with difference in depth in individual mines is less marked, yet noteworthy. Ore shoots of gold, silver, and zinc have clearly segregated by oxidation. The district is remarkable for an unusually low water level and great depth of oxidation. The water level in igneous rocks is 200 to 700 feet below the surface; in sedimentary rocks water stands from 1,650 to 2,400 feet below the surface, according to the elevation of the shaft, and broadly speaking is found about 200 feet above the level of Utah Lake, or at an elevation of 4,800 feet. Explorations in ore below water level have been undertaken only in the Gemini mine, where partly oxidized ores have been found about 200 feet below the present water level. The ore as deep as level 21 of the Mammoth mine is oxidized and honeycombed like a gossan.

The oxysalts formed in lead and zinc mines consist of anglesite, cerusite, plumbojarosite, smithsonite, calamine, and hydrozincite, while the copper mines yield many copper arsenates, malachite, and azurite, more rarely cuprite and native copper. Silver is present as argentite, cerargyrite, and native metal, and some rich oxidized ores show native gold.

Covellite and chalcocite are found everywhere in the oxidizing copper ores, though nowhere in great masses. They are not remnants of an older sulphide zone but are developed in all parts of the oxidized zone near the surface as well as near the water level. This condition, according to Lindgren, is caused in part by the scarcity of pyrite, by the neutralization of such sulphuric acid as is formed by $CaCO_3$ and in part also by the great amount of oxygen necessary for the oxidation of enargite.

The formation of arsenates and chalcocite in solutions containing oxygen and calcium carbonate from the limestone surrounding

the jasperoid zone of the deposits is indicated by the following formula:

$$\underset{\text{(Enargite.)}}{3Cu_2S.As_2S_5}+30+H_2O+7CaCO_3=\underset{\text{(Olivenite.)}}{4CuO.As_2O_5.H_2O}+\underset{\text{(Chalcocite.)}}{Cu_2S}+7CaSO_4+7CO_2.$$

Chalcocite and covellite form dull bluish or sooty spots in the enargite, famatinite, galena, or zinc blende. In thin section, chalcocite appears as a marginal alteration in these primary ore minerals, particularly in the enargite, and blades of covellite develop later in the chalcocite. Along fractures copper arsenates are forming between the marginal zones of chalcocite and the arsenates themselves contain ribbons of chalcocite often delicately contorted. Here the chalcocite must have formed practically at the same time as the arsenates.

Covellite forms during the oxidation of galena, which contains some primary copper mineral. Along the margin, where the galena changes to anglesite, the latter mineral contains plates of covellite embedded in it and very clearly replacing it. In the same specimens residual masses of galena in anglesite are surrounded by a narrow replacement ring of covellite. Crystallized covellite is sometimes found in druses associated with anglesite. Galena is recrystallized in part during the formation of anglesite. Ruby silver occurs in drusy cavities and is regarded as a secondary mineral. Secondary argentite is common in the richer silver ores.

In some of the copper mines the average oxidized ore contains gold up to $10 or $15 per ton, but in addition certain parts of the shoots are very much richer, containing 1 to 5 ounces per ton. These rich gold ores in part contain visible gold of deep-yellow color the streak of which indicates purity. The secondary nature is apparent from its deposition between quartz grains or as thin flakes on joints. In the ores where such gold stopes occur there is always more or less manganese.

In the Gemini mine just above and below the water level the ore is principally sulphides. It is extremely rich, containing from 100 to 3,000 ounces of silver to the ton. It occurs in a breccia of dark jasperoid and dolomite. Much of the jasperoid is similar to the ordinary normal sulphide ore and contains finely disseminated galena, pyrite, and zinc blende. The ore minerals occur as replacements and filling in the cement of this breccia and sometimes directly replace the dolomite, a mode of occurrence unknown elsewhere in the district, except at some outlying mines in North and East Tintic.

The ore minerals consist of coarse galena in part in intimate "eutectic" intergrowths with a mineral, which is probably pearceite ($Ag_9(Cu)AsS_6$). Inclosed in the galena are rounded, concentric spherulites of zinc blende and of a very dense marcasite or pyrite;

crystallized marcasite occurs in the same shoot. The deposition was accompanied by a little quartz as small clear crystals and seemingly the last mineral to crystallize. The spherulites of zinc blende contain droplike inclusions of galena.

During the partial oxidation to which this ore has been exposed covellite and native silver have formed from the pearceite and the galena has yielded a little cerusite.

The genesis of zinc carbonate ores in the Tintic district is discussed on page 387.

EUREKA, NEVADA.

The Eureka district,[1] in eastern Nevada, is an area of Paleozoic quartzites, limestones, and shales, which were intruded, probably in late Mesozoic time, by granite, granite porphyry, and quartz porphyry. Subsequently, probably in the Tertiary period, the sedimentary rocks were intruded by great igneous bodies of andesitic composition and covered in places by rhyolite and basalt. The beds are thrown into open folds and the dominant structure is a fault mosaic, the principal faults being of the normal type.

The ores occur in sedimentary rocks belonging to the Cambrian, Ordovician, and Devonian periods. Through a section involving 17,000 feet of deformed strata they have been deposited in sufficiently large bodies to encourage mining exploration.

According to Curtis,[2] the ore bodies are chiefly replacements of fractured limestones and include lodes, stocks, and bedding-plane deposits. The elevation of the region is from 6,000 to 7,500 feet above the sea, but neighboring peaks are higher. The climate is arid and the water level deep. On a section by Curtis through the Jackson, Eureka Consolidated, and Richmond shafts,[3] the water level is shown at a depth of 500 feet in the Jackson and from 1,000 to 1,200 feet in the Richmond shaft.

The larger ore bodies, according to Curtis, are capped by caves or are in some way connected with caves or fissures, developed by solution, and the fall of rock into the openings has caused further fissuring. Since this action took place the ore has in many places been redistributed by the flow of underground waters. The ore above the water level is composed principally of the minerals galena, anglesite, cerusite, mimetite, and wulfenite, with very little quartz and calcite, the gangue being for the most part hydrated oxide of iron. The ore carries also considerable gold and silver and some zinc, which occurs probably as carbonate and silicate. The ore

[1] Hague, Arnold, Geology of the Eureka district, Nevada: U. S. Geol. Survey Mon. 20. 1892.

[2] Curtis, J. S., Silver-lead deposits of Eureka, Nev.: U. S. Geol. Survey Mon. 7, 1884.

[3] Idem, Pl. III.

below the water level is composed chiefly of pyrite, arsenopyrite, galena, zinc blende, and a few other sulphides, as well as silver and gold. According to Curtis the oxidized ore grades into the sulphide ore. At some places altered ore is found below the water level, and Curtis supposed that the water level was recently elevated. The development of mimetite, chloro-arsenate of lead, as stalactites in the oxidized zone, is of interest. Zinc blende is found to some extent in upper parts of the mines, according to Curtis, and is of common occurrence in the lower workings in connection with pyrite and galena. The deposits had produced over $60,000,000 in silver and gold and 225,000 tons of lead in 1882. More recently enormous bodies of low-grade ferruginous gold ore have been mined in the shattered and altered limestones that surround the old silver stopes.

PIOCHE, NEVADA.

The deposits of Pioche, Nev.,[1] are in a faulted area of quartzites, limestones, and shales which are cut by an acidic porphyry intrusive. The most important deposits, some of which have been very productive, are near the intrusives. They fill fissure veins in the quartzite and limestone and the ores are more abundantly developed in the quartzite. They were stoped at the surface and averaged about $150 a ton. Ores consisting of silver chloride and sulphide and lead carbonate extended to water level, where the oxidized ore gave place to sulphides and large amounts of zinc also entered. At this depth, according to Pack,[2] the vein was generally strong and persistent, but no valuable deposits were in sight when the property was abandoned, even though prospecting had been very extensive.

In recent years some other large productive deposits have been developed. Of these I have no exact knowledge.

ROSSLAND, BRITISH COLUMBIA.

Rossland, British Columbia, is in the Trail Creek district, a short distance north of the international boundary. The country is glaciated and the altitude of the principal deposits is about 3,400 feet above sea level. The rocks exposed[3] include Carboniferous limestone, quartzites, and shales with interbedded tuffs, ash beds, and lavas. Above this series are volcanic agglomerates and lavas. Intruding these rocks are masses of monzonite, granodiorite, nepheline syenite, etc.

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[1] Pack, F. J., Geology of Pioche, Nev., and vicinity: School of Mines Quart., vol. 27. pp. 285–312, 365–386, 1906.

[2] Idem, p. 372.

[3] Brock, R. W., Preliminary report on the Rossland, B. C., mining district, Canada Geol. Survey, 1906. Drysdale, C. W., Geology and ore deposits of Rossland, British Columbia: Canada Geol. Survey Mem. 77, 1915.

The principal deposits are fissure fillings, silicate replacements, fractured zones, and impregnations. The most important lodes have steep dips. These lodes are intricately faulted and many of the faults follow or are followed by basic dikes. The deposits carry commercial amounts of copper, gold, and silver.

The gangue minerals are biotite, quartz, calcite, tourmaline, amphibole, chlorite, and garnet; the sulphides include pyrrhotite, chalcopyrite, pyrite, arsenopyrite, marcasite, gold, and other minerals.

In certain gold-bearing quartz veins the gold and chalcopyrite are intimately related and there is a notable concentration of gold near the surface.

The ore shoots in the cupriferous precious-metal lodes extend downward 50 to 500 feet. One shoot averaged 150 feet long and 56 feet thick and was worked downward 500 feet. There is very little oxidation above these deposits and no secondary chalcocite zone. The values of shipments decrease as greater depths are reached, but this decrease may be due to improvement of conditions which permits profitable extraction of lower-grade material.

ST. EUGENE MINE, BRITISH COLUMBIA.

The St. Eugene mine, in the East Kootenay district, near Lake Moyie, British Columbia, is in the largest lead-producing region of Canada. This region is mountainous and is in moderately high latitude and is therefore of particular interest, for the workable ore shows a relation to the present topography that indicates appreciable secondary concentration. The deposit of the St. Eugene mine affords one of the best examples of sulphide enrichment that I have noted in Canada. The following data are from reports by S. J. Schofield[1] and from a communication received through the courtesy of Mr. R. W. Brock, then director of the Geological Survey of Canada.

The claims operated by the principal company include two veins, which strike east and dip 70° S. They are about 600 feet apart and the developments extend through a vertical range of 2,100 feet. The lower workings are over 100 feet below the level of Lake Moyie. The two main veins are connected by a series of important cross veins, most of which meet the main veins at acute angles. These cross fissures, the spaces between which are not uniform, are locally termed "avenues." Most of the ore bodies are in the fractured and folded area along and between the main veins, and in places large ore shoots occur near or at the places where the avenues meet the

[1] Schofield, S. J., Reconnaissance in East Kootenay: Canada Geol. Survey Summ. Rept. for 1911, 1912, pp. 158–164. The origin of the silver-lead deposits of East Kootenay, British Columbia: Econ. Geology, vol. 7, pp. 351–362, 1912.

main veins. Very little displacement was observed along the main fissures, although the strata are slightly folded or bent near the fissures. The country rocks consist of argillaceous quartzites and purer heavy-bedded quartzites of the pre-Creston, the oldest known subdivision of the Purcell series of Schofield, which here form the axis and eastern limb of an anticline. The ore bodies are replacement deposits in the massive purer quartzites of the pre-Creston formation. The ore consists of galena, both fine and coarse grained, associated in places with zinc blende and pyrite. The gangue, which is small in amount, consists of garnet, anthophyllite (a variety of amphibole), and a little quartz, the quartz being very prominent where a vein pinches in the argillaceous quartzites. Locally the wall rock near the ore bodies shows strong metamorphism by the development of garnet and anthophyllite. The deposit, like deposits in the Coeur d'Alene district, contains a little magnetite and pyrrhotite.

A vertical projection or stope sheet supplied by Mr. Brock shows workings along the hill for 4,900 feet. The slope of the hill is about 25°. Thirteen tunnels, one above another, are driven to the ore zone. Some of these tunnels are 2,000 to 3,000 feet long, but all the stopes appear to be within 1,500 feet of the surface, as measured on a level, or somewhat less than 800 feet from the nearest points on the surface. The distance from the surface to which most of the ore shoots were followed is practically uniform. Below the level of the lake the workings did not extend so deep. At depths the fissures tighten, the ore becomes less concentrated, and zinc blende becomes relatively more abundant, so that the ore is no longer of commercial grade. At the junction of the "avenues" and main vein and nearer the surface were large bodies of clean shipping ore. Elsewhere the ore was concentrating ore. Mr. Brock informs me that a similar relationship between present surface and the ore bodies is noticeable at many points in the Slocan.

PHILIPSBURG, MONTANA.

The Philipsburg quadrangle is an area of sedimentary rocks ranging in age from pre-Cambrian to late Cretaceous, with intrusions of granodiorite and related rocks, probably belonging to the same period of intrusion as that of the Butte quartz monzonite and other batholiths in Montana. The most important ore deposits in this quadrangle are those of the Granite-Bimetallic and Cable mines.

The Granite-Bimetallic mine[1] is working a strong fissure vein in granodiorite, which carries chiefly silver but also an important amount of gold. There is conclusive paragenetic evidence of the enrichment of silver below the water level, and the rich silver ore

[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 202, 1913.

carries also more gold than the low-grade silver ore in the bottom of the mine. The outcrop of this deposit carried some silver but very little gold, and after the discovery the location was allowed to lapse by reason of the small assay returns from the gossan. Richer ore with secondary cerargyrite, native silver, and ruby silver in cracks across the older sulphides appeared in considerable amount 200 to 400 feet below the surface and extended to depths of 800 or 900 feet. The shoot of high-grade ore, which extended for about a mile along the strike of the deposit, followed, in a broad way, the present rugged surface. (See fig. 17, p. 267.) The primary sulphides include pyrite, stibnite, arsenopyrite, galena, sphalerite, and others. The quartz gangue is rich in manganese as rhodochrosite and rhodonite. No pyrrhotite was noted, but zinc blende is abundant at several places in the primary ore below the richer sulphides. Some migration of gold has undoubtedly taken place. No associated placers have been developed.

At the Cable mine[1] the deposits are included in a long, thin block of limestone, in contact on either side with quartz monzonite. The principal minerals are calcite, quartz, pyrrhotite, pyrite, magnetite, and chalcopyrite, with chlorite, muscovite, and other silicates. At one or two places small traces of manganese dioxide have been noted in the oxidized ore, but it is very much less abundant than in the deposits of the Granite-Bimetallic type. This deposit yielded important placers. Good ore was found at or very near the surface and, according to the best obtainable data, the tenor increased somewhat for a short distance below the surface. Some concentration has taken place by the removal of calcite and other valueless material more rapidly than gold, but there is no evidence of enrichment in gold below the water table. The conditions indicate that the gold has not been extensively transported since the deposit was formed.

NEIHART, MONTANA.

The Neihart district, Montana,[2] is a region of Archean granite and pre-Cambrian quartzite with intrusive diorite and porphyry. The deposits are silver-bearing fissure veins, which in depth carry considerable sphalerite, pyrite, and galena. Superficial oxidation is not extensive, and there are no great zones of carbonates and oxidized ore. The Broadwater vein is partly oxidized to a depth of 170 feet and in pipes and fissures to even greater depths. Below the oxidized ore were large bodies of secondary silver sulphides, consisting of polybasite, pyrargyrite, pearceite, and "sooty sulphide ores," much of this ore running 200 to 1,000 ounces per ton. The rich silver

[1] Emmons, W. H., and Calkins, F. C., op. cit., p. 221.

[2] Weed, W. H., Geology of the Little Belt Mountains, Mont.: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, pp. 271–581, 1900.

minerals occur in cracks in the primary ore or coat fragments of that ore. Manganese oxides abound.

The zones of impoverishment, of enrichment, and of unaltered primary sulphides recognized in the case of the copper veins are clearly present here, though the uppermost is of limited extent, and the zones are not so sharply or definitely separated from one another as they are in copper deposits, owing to the later fissuring of the vein filling allowing the secondary enrichment to be mixed with the unaltered sulphides. * * * In the Neihart ores polybasite seems to show an alteration to pyrargyrite and pyrite, and the former in turn changes to native silver in the upper zone.[1]

A specimen collected by Weed from the 300-foot level of the Big Seven mine, Neihart region, was polished and studied by E. S. Bastin.[2] This ore consists principally of galena, chalcopyrite, sphalerite, barite, dark-gray quartz, and brown carbonate. One side of the specimen is the wall of an open fissure, and along this side there is a coating of polybasite and pyrargyrite, in places a quarter of an inch thick. The two silver sulphides appear essentially contemporaneous and are plainly secondary. Portions of the original galena adjacent to the open fracture have been metasomatically replaced by polybasite. The replacement by polybasite is shown between the quartz and galena, between different galena crystals, and along cleavages of galena.

GEORGETOWN, COLORADO.

The Georgetown district, Colorado, is a rugged area of gneisses and schists, which are cut by Tertiary intrusives of varied composition. Several thousand feet of overlying rocks, according to Spurr, Garrey, and Ball,[3] have been eroded since the veins were formed. Some of the valuable minerals of the eroded portions have been redeposited in the portions remaining.

The zone of complete oxidation is 5 feet to 40 feet deep. In the silver-lead deposits the minerals on the lower levels are chiefly zinc blende and galena, with pyrite, chalcopyrite, and a little silver and gold. Rich soft sulphides are found, especially along cracks and watercourses, and are of secondary origin, having evidently been concentrated from the leaner ore by descending waters. They occur down to considerable depths from the surface but in decreasing quantity. The older and typically more massive ores in which they have formed contain usually very much less silver and also less gold. For example, secondary sulphides which contain 200 to 300 ounces of

[1] Weed, W. H., The enrichment of gold and silver veins: Am. Inst. Min. Eng. Trans., vol. 30, p. 446, 1901.

[2] Bastin, E. S., Metasomatism in sulphide enrichment: Econ. Geology, vol. 8, p. 59, 1913.

[3] Spurr, J. E., Garrey, G. H., and Ball, S. H., Economic geology of the Georgetown quadrangle, Colorado: U. S. Geol. Survey Prof. Paper 63, p. 145, 1908.

silver have been formed by this concentration process from primary ore which carries only 20 to 30 ounces.

Below the zone where soft secondary sulphides occur and irregularly overlapping the lower portion of this zone the rich ores contain polybasite, argentiferous tetrahedrite, and ruby silver, better crystallized and more massive than the pulverulent sulphides but also subsequent in origin to the massive galena-blende ore. These richer ores diminish in quantity as depth increases, though gradually and irregularly, so that the lower portion of the veins contains relatively less silver and lead. The best ore in most veins has been found in the uppermost 500 feet, although good ore extends locally down to 700 or 800 feet, and in the Colorado Central and to a minor extent in other veins down to a thousand feet or more.[1]

BRECKENRIDGE, COLORADO.

The fundamental rocks in the Breckenridge region, Colorado, as stated by Ransome,[2] are granites, pegmatites, gneisses, and schists of pre-Cambrian age. The oldest sedimentary rocks, which rest directly on the pre-Cambrian, are red sandstones and shales, supposed to be of Triassic or of Permian age. Apparently conformable above them is the Dakota quartzite, with some gray shale, which is overlain by a thick formation of Upper Cretaceous shales. The sediments and the pre-Cambrian rocks are intruded by monzonitic porphyries, which occur mainly as sills.

The primary deposits, according to Ransome, include veins of a zinc-lead-silver-gold series, stockworks and veins of a gold-silver-lead series, and the gold veins of Farncomb Hill. The placers of the district have been important producers of gold.

The Wellington veins afford the chief examples of the zinc-lead-silver-gold series, the filling of which consists mainly of sulphides, quartz in notable quantity being absent from most of them. In the Wellington mine the principal constituents of the ore are galena, sphalerite, and pyrite in various proportions. Even along the outcrops of the veins of the Wellington group most of the deposits carry galena in the claylike product resulting from thorough oxidation, but the change to essentially sulphide ore generally takes place at depths of less than 300 feet. The depth of the oxidized zone, however, varies, being greatest in general near the crest of the ridge in which the ore bodies occur and least along the lower slopes.

The normal sequence from the surface down appears to be (1) a soft, heavy yellowish claylike ore consisting largely of earthy cerusite and containing residual nodules of galena; (2) a lead-silver ore in which the galena is only in part oxidized, while the pyrite has been for the most part changed to limonite

[1] Spurr, J. E., Garrey, G. H., and Ball, S. H., op. cit., p. 144.

[2] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, pp. 25–26, 1911.

and the sphalerite altered to smithsonite and limonite, with removal of much of the zinc in solution; and finally (3) a lead-silver-zinc ore in which galena predominates and in which the early stages of oxidation are indicated by the formation of a little spongy smithsonite, or "dry bone," as the miners call it, at the expense of the zinc blende.[1]

A notable feature of the oxidized ores is their general high content of lead and silver as compared with the sulphides beneath. In some mines this difference was so great that their owners after extracting ore profitably to the base of the oxidized zone found the sulphides of so low a grade that they abandoned work. Here and there the oxidized ores also show a noteworthy concentration of gold even where the sulphide ores below contain only negligible quantities of that metal. Thus in the Helen mine, on the south side of French Gulch, some gold ore was found near the surface, although the latest and deepest workings have exposed nothing but a little sphaleritic zinc ore. In the Juventa mine, which produced some good oxidized ore to a depth of 200 feet and was then abandoned, wire gold is said to have been found.

It is believed that a large proportion of the galena is the result of downward concentration by atmospheric water, which, after percolating with comparative rapidity through the oxidized zone to the local ground-water level, thence moved more slowly down through the sulphides, emerging finally along the bottoms of the main valleys. Although some sphalerite is younger than other sphalerite, it is not surely a deposit of sulphate waters. Iron is deposited as an impure siderite in veinlets traversing the sulphide ores or as the lining of vugs in these ores. Additional iron issues in springs after performing its work of enrichment. Silver, according to Ransome, generally keeps close to the lead, and gold appears to accumulate in the zone of oxidation rather than at greater depths. In general profitable operations did not extend below 300 or 350 feet in depth.

The Farncomb Hill veins immediately below the zone of oxidation consist of pyrite, chalcopyrite, sphalerite, galena, calcite, and gold. Some wire gold has been found in the unoxidized vein material but not far below the zone of general weathering, and the principal concentration of the native metal is connected with oxidation.

Ransome[2] says:

Two intimately related processes appear to have been effective in enriching these veins. These, in the order of their action at one place, were (1) enrichment by solutions depositing calcite, galena, gold, and perhaps sphalerite below the zone of oxidation and (2) enrichment in the zone of oxidation by solution and redeposition of the gold.

It is clear that during the weathering of these veins the gold was acted on by some very efficient solvent, for otherwise it would be impossible to account for

[1] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Survey Prof. Paper 75, p. 134, 1911.

[2] p. 169.

the large crystalline masses of gold characteristic of the hill. These could not have been deposited in the veins as part of their original fillings, for they are limited to the oxidized zone, and the once very productive placers below the hill show that this zone can not coincide with originally rich upper portions of the veins. Evidently the original tops of the veins have been eroded away and their contained gold in part has been strewn along the ravines and down the main valleys and in part has seeped down in solution along the fissures and been deposited in segregated masses. Active as solution must have been, erosion apparently was overtaking it; at least the richness of the placers proves that the gold was not carried down and redeposited fast enough to escape the forces of mechanical disintegration.

Ransome states that a manganiferous carbonate occurs in the Wire Patch mine of Farncomb Hill, and sphalerite from the Silver vein showed some manganese, but some oxidized material from the Reveille showed none. It is not known whether the mine water carried appreciable chloride, but the experiments of Brokaw (p. 306) indicate that under some conditions a faint trace of chlorine is effective in the solution of gold. In connection with abrupt impoverishment in depth, attention should be called also to the mineral association of these ores and to experiments previously cited showing the rapidity with which acid solutions are reduced by sphalerite and auriferous chloride solutions are neutralized by calcite. With both calcite and sphalerite the conditions for rapid precipitation of gold are very favorable.

GILPIN COUNTY, COLORADO.

Certain gold and silver veins in Gilpin County, Colo.,[1] as in adjacent parts of Clear Creek and Boulder counties, are workable only in their upper parts and show clear evidence of enrichment of silver. The original minerals are galena, sphalerite, chalcopyrite in a gangue of quartz, rhodochrosite, and barite. Secondary minerals are polybasite, proustite, galena, chalcopyrite, and more rarely stephanite. The country is rugged and the ground-water level is high. Near Lawson, in the Little Giant mine, the water level was within 60 feet of the surface, and in general the water level was not more than 75 feet deep. The richer ores extend much deeper, and there is evidence of secondary sulphide enrichment 500 to 700 feet below the surface. The primary ores below that depth are of low grade and carry less than 20 ounces a ton in silver. The secondary sulphides fill cracks in and replace the primary sulphides and quartz. The ready replacement of quartz and galena suggests the action of alkaline solutions in these calcitic veins. As in some other districts, the source of the arsenic and antimony in the secondary minerals is uncertain. No original minerals containing these metals are named.

[1] Bastin, E. S., Metasomatism in downward sulphide enrichment: Econ. Geology, vol. 8, p. 51, 1913.

RICO, COLORADO.

The rocks of Rico, Colo.,[1] include Paleozoic limestones, sandstones, and shales, which are cut by dikes and laccolithic sheets of monzonite porphyry. The ore deposits include fissure veins and ribbon-like masses, which make out in limestone from the fissure veins where the latter cross the contact of limestone with overlying shale. In the lower levels of the mines, some 200 feet below the "contacts," the ore is mainly quartz, pyrite, and chalcopyrite. In raising on the veins rhodochrosite, galena, sphalerite, and tetrahedrite become prominent. Upward, toward the "contact," the proportion of metallic minerals steadily increases, and the ore becomes much richer in gold and silver. Irregular nuggets and sheets of argentite, polybasite, and stephanite are found. Occasionally pyrargyrite, proustite, and native silver appear. Rhodochrosite, on the other hand, is almost never found in the zone immediately below the shale, although it is abundant in the vein material lower down.

LAKE CITY, COLORADO.

The silver-lead deposits of Lake City,[2] in southwestern Colorado, are in an area of Tertiary flows and tuffs of the Silverton volcanic series, which consists of andesites, rhyolites, latites, and basalts. These are cut by intrusions of rhyolite and quartz latite and by quartz monzonite porphyries.

The deposits are narrow fissure veins and some fill rudely parallel fissures. Their vertical range, according to Irving and Bancroft, is over 5,000 feet, and in their lower levels the primary minerals are chiefly quartz, galena, zinc blende, and pyrite. The ores formed at shallower depths include also tetrahedrite, rhodochrosite, barite, and jasperoid. The mineralization was probably effected by solutions connected genetically with the quartz monzonite intrusion or with some closely related deeper rock.

Many of the lodes are greatly fractured, and the conditions in this rugged country are favorable to deep circulation. Erosion is rapid, however, and the oxidized zone is not deep, extending generally not more than 100 or 200 feet below the surface. This zone contains iron oxides and sulphates, copper carbonates, and considerable anglesite, with some native copper and silver. Cerusite is not abundant.

The secondary silver minerals are chiefly pyrargyrite and galena but include some chalcocite and possibly proustite. Native gold, though not common in the oxidized ore, is present in the upper part

[1] Ransome, F. L., The ore deposits of the Rico Mountains, Colo.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 229–398, 1901. Farish, J. B., The ore deposits of Newman Hill: Colorado Sci. Soc. Proc., vol. 4, pp. 151–164, 1892. Rickard, T. A., The Enterprise mine, Rico, Colo.: Am. Inst. Min. Eng. Trans., vol. 26, pp. 906–980, 1896.

[2] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, 1911.

of the zone of sulphide enrichment. Of the total production of all metals, having a value above $7,000,000, about one-sixth is gold. The table showing the metal production of the district indicates a fairly constant proportion in the annual production of gold and silver. The abundance of sphalerite in the primary ore would seem to favor relatively rapid precipitation of the metals by descending solutions. Some of the secondary ore shoots, however, have a wide vertical range, but such a distribution of the richer ore has been greatly favored by the very rugged topography. At the Moro mine the secondary sulphides are found nearly 500 feet vertically below the surface, but the slope is between 30° and 40° and the circulation is presumably vigorous. The reactions precipitating the metals seem to have been relatively rapid. As stated by Irving and Bancroft,[1] zinc blende has very generally exerted an extensive effect in reprecipitating the downward-moving sulphates in the form of secondary sulphides.

CREEDE, COLORADO.

The Creede district,[2] in Mineral County, Colo., lies within the great Tertiary volcanic area of the San Juan Mountains, and no rock formations other than Tertiary flows and intrusives are exposed within a radius of several miles. Eleven formations are recognized, each consisting of one or more flows of rhyolite, andesite, or basalt, or of tuffs. Lake beds made up of water-laid fragments of rhyolite and extensive deposits of travertine lie south of Creede. The lava beds are intruded by dikes of quartz porphyry, quartz monzonite porphyry, and basalt.

The lava flows are deformed by complicated block faulting, some of the faults having throws of more than 1,000 feet. Most of the deposits are in veins formed in fissures produced by normal faulting, but some of them follow porphyry dikes. The principal deposit, the Amethyst lode, is developed for about 9,500 feet along the strike, and has been exploited to depths of 1,000 to 1,400 feet below the surface. It strikes about N. 22° W. and dips southwest 50° to 65°. The rocks show much postmineral fracturing.

The minerals that form the unoxidized ore in the lower levels of the Amethyst vein include zinc blende, galena, pyrite, chalcopyrite, gold, barite, and amethystine and white quartz. In the country rock along the vein secondary quartz, chlorite, adularia, and some sericite are developed. Thuringite, a chlorite rich in iron, appears to occur in the filled portion of the vein as well as in the country rock near it. This mineral, unusual in western silver deposits, is one of the most

[1] Irving, J. D., and Bancroft, Howland, op. cit., p. 64.

[2] Emmons, W. H., and Larsen, E. S., A preliminary report on the geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. 530, pp. 42–65, 1913.

abundant gangue minerals. Hydrothermal metamorphism is not pronounced except near the vein.

The most valuable deposits of silver, the most important metal in this district, were found 200 to 700 feet below the surface, but wire silver was mined at depths below 1,000 feet.[1] Some of the richest silver ore is evidently secondary and consists of red jasper with abundant native silver. (See fig. 16, p. 267.)

Stringers of black manganese oxide cutting unoxidized sulphide ore extend downward to depths of nearly 1,000 feet. In the Happy Thought mine, on the Amethyst vein, between levels 6 and 7, a body of partly oxidized ore composed of galena, zinc blende, copper carbonates, cerusite, and anglesite carries a conspicuous amount of manganese dioxide, which coats the copper sulphides and occurs in fractures cutting the partially oxidized ores. A considerable body of this ore yielded $20 a ton in gold, which indicates notable enrichment, since the average content of gold in the mine is about $2 a ton.

COMSTOCK LODE, NEVADA.

The Comstock lode[2] is a broad fault zone in late Tertiary rocks. The ore shoots occur here and there in this zone, which is developed more than 4,000 feet below the surface.

King[3] says:

> Quartz forms the * * * gangue in the Comstock lode. Those small masses of carbonate of lime which occur, intermingled with quartz, in the Gold Hill and Hale & Norcross lower levels are rather to be considered an included mineral of accidental occurrence than as a true gangue. With the exception of small quantities of silver minerals contained in the clay sheets where they are placed in close contact with the bonanza, the whole silver tenure of the lode is contained in the bodies of quartz. The ore itself is composed of native gold, native silver, silver glance, stephanite, rich galena, occasional pyrargyrite, horn silver, and, with extreme rarity, sternbergite. Intimately associated with these occur iron and copper pyrites and zinc blende. Of these, pyrargyrite and horn silver are rarities; polybasite and sternbergite, in recognizable crystals, occupy a few scattered localities; stephanite, in defined crystallizations, has been found in nearly every bonanza, but the main body of the ore is a confused semicrystallized association of native gold and silver, vitreous silver ore, rich galena, copper and iron pyrites, and zinc blende.

In general the bonanza ore is pretty uniformly disseminated through the quartz. Large, solid accumulations are rarely found. The silver minerals ordinarily lie in masses about the size of a hen's egg. In the central portions of bonanzas there is usually a somewhat denser arrangement of ore. It is evident, from the manner in which

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[1] Emmons, W. H., and Larsen, E. S., op. cit., p. 58.

[2] King, Clarence, The Comstock lode, in Hague, J. D., Mining industry: U. S. Geol. Expl. 40th Par., vol. 3, pp. 11–96, 1870. Church, J. A., The Comstock lode, New York, 1879. Becker, G. F., Geology of the Comstock lode and the Washoe district: U. S. Geol. Survey Mon. 3, 1882. Reid, J. A., The structure and genesis of the Comstock lode: California Univ. Dept. Geology Bull., vol. 4, pp. 177–199, 1905.

[3] King, Clarence, op. cit., p. 79.

the ore itself is broken and dislocated, that the dynamic action which powdered the quartz occurred after it was charged with ore.

Since the period of crushing additional quartz and ore are said to have been introduced into the fissure in small quantities. In a few places, as in the 800-foot level of the Yellow Jacket mine, broken fragments of quartz, themselves containing ore, have been recemented by sheets of stephanite which have penetrated the cracks, and over the stephanite a secondary growth of quartz crystals has taken place, and these quartz crystals themselves are again coated with a fine varnish of silica.[1]

Analyses of ore from the lower workings of the Savage and Kentuck mines (1869) gave zinc sulphide 1.75 and 0.13 per cent, respectively. Ores from "middle depths" of the California and Ophir mines gave 12.85 and 14.45 per cent of zinc.

Like King, Becker notes that there were clearly two periods of movement, one before the deposition of the primary ore and one after it. The later movement, mainly parallel to the lode, gave conditions for an active circulation of water after the primary deposition. According to Becker,[2] "it is possible that the seams of rich ore in the great bonanza represent a deposition posterior to the final cessation of movement," and "it is also by no means impossible that some of the richer ores have been redeposited, forming at the expense of surrounding bodies of lower grade." As already remarked, analysis of the vadose water of the Comstock shows that it contains both gold and silver. It is noteworthy that this water contains much manganese, presumably as sulphate. Some associated placers were developed, but they are of very subordinate value compared with that of the lode. Oxidation extended downward to a depth of 500 feet. According to King,[3] "a zone of manganese oxide occupies the entire length of the lode from the outcrop 200 feet down." The upper part of this manganiferous zone was not of high grade in general, especially in its uppermost portions. The longitudinal projections[4] show that many of the stopes carried from below stop some distance below the surface.

Von Richthofen (quoted by Becker) says that "the proportion of gold to silver decreased during the early period of working the lode but is now (1865) on the increase again." Presumably silver at the very surface was leached more rapidly than gold. The vadose waters, as shown by Reid,[5] are rich in sulphate, and his analyses, as well as others, show the presence of chlorides in appreciable amounts. The conditions appear to have been favorable for the migration of

[1] King, Clarence, op. cit., p. 81.
[2] Becker, G. F., op. cit., p. 273.
[3] King, Clarence, op. cit., p. 75.
[4] Becker, G. F., op. cit., atlas sheets X–XII.
[5] Reid, J. A., op. cit.

both silver and gold in the upper levels, even in the comparatively short time that has elapsed since the primary ores were deposited. The bonanza ore below consisted largely of stephanite, polybasite, argentite, and other minerals.

I have no detailed descriptions of the character and position of the richest ores, but Eliot Lord[1] states that the "Big Bonanza," an enormously rich ore body in the lode, extended below the fifteenth level. Possibly some of the richer ore bodies extended still deeper, but it is well known that rich ore was more abundant in the upper than in the lower levels. The deposits in the upper levels yielded, according to Richthofen, from $70 to $107 a ton, whereas in later years the average value of the ore was not more than $37 a ton.

It thus appears that the evidence of the Comstock lode, from the surface down, is favorable to the hypothesis that extensive solution and deposition of gold and silver have taken place.

The proportion of gold to silver was presumably higher near the surface and in the lower part of the lode than in the middle part. When Richthofen made his report he estimated that to the close of 1865 the lode had produced $15,250,000 in gold and $32,750,000 in silver (gold equals 47 per cent of the silver); whereas Becker reports the amount recovered from 1865 to 1881 as $87,121,988 in gold and $105,548,157 in silver (gold equals 83 per cent of the silver).

The relation of "horn silver" to the surface is different from that shown in "chloride mines." According to King,[2] silver chloride is accidental, although rare small crystals were found at the outcrop of the Gold Hill group and elsewhere.

TONOPAH, NEVADA.

The deposits at Tonopah, Nev., are silver-gold replacement veins in andesite. They are of middle or late Tertiary age but possibly somewhat older than the Comstock lode. Placers are not developed. The primary ore according to Spurr[3] is composed of quartz, adularia, sericite, and carbonates of lime, magnesia, iron, and manganese, with argentite, stephanite, polybasite, chalcopyrite, pyrite, galena, silver selenide, and gold in an undetermined form. Pyrrhotite is not listed. According to Spurr, a little zinc sulphide is present, but Burgess[4] does not list sphalerite as a vein mineral.

The zone of oxidation extends to greater depth in the more highly fractured places, and for this reason the brittle and more broken

[1] Lord, Eliot, Comstock mining and miners: U. S. Geol. Survey Mon. 4, p. 311, 1883.
[2] King, Clarence, op. cit., p. 82.
[3] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 90, 1905.
[4] Burgess, J. A., The halogen salts of silver and associated minerals at Tonopah, Nev.: Econ. Geology, vol. 6, pp. 13–21, 1911.

lodes are more deeply oxidized than the wall rock. The Mizpah vein is for the most part oxidized to a depth of 700 feet. Standing ground water is lacking. The oxidized ore contains limonite and manganese dioxide, with plentiful horn silver and some bromides and iodides of silver. The so-called oxidized ore from the outcrop down is, according to Spurr, a mixture of original sulphides (and selenides), together with secondary sulphides, chlorides, and oxides. At a depth of 500 feet (in the Montana Tonopah mine) good crystals of argentite, polybasite, and chalcopyrite have been formed freely in cracks and druses of the sulphide ore. These minerals are later than the massive ore, but it can not be shown that they were not deposited upon it by ascending waters. The deposit of dark ruby silver (pyrargyrite) is different, however, for it is formed in cracks in the oxidized ore, and some argentite fringes minute particles of horn silver as if secondary to it. The evidence, therefore, as stated by Spurr, favors the view that the secondary sulphides in the oxidized zone originated from descending surface waters, and probably part of the sulphides in druses in the sulphide ore have a similar origin.

The waters that descend through the oxidized zone carry sulphates and chlorides, and "wad" is plentiful; but judging from the fairly constant proportion of gold to silver (about 1 to 100 by weight) there has been little selective migration of gold and silver during oxidation, although the vein has been enriched somewhat by downward penetration of the metals leached from the outcrop as it was eroded. The rich ore shoots, though partly oxidized, seem to be in the main original without thorough rearrangement. According to Spurr, this may be ascribed in part to the relatively scanty supply of water in this arid region.

COBALT, ONTARIO.

Cobalt,[1] in the Nipissing district, northern Ontario, is on the great ancient peneplain which extends over much of Ontario and the surrounding region. The country is hilly, but the relief is not great. The climate is cold and moderately moist. The recent glaciation is clearly evident, but drift is generally thin or absent.

The basement rocks are the Keewatin series, a complex of metamorphosed basic igneous rocks, usually known as greenstones, which includes also some rock of sedimentary origin. The eroded surface of the Keewatin is overlain by Huronian conglomerates, graywacke, and other metamorphosed sedimentary rocks. A quartz diabase sill some 500 feet thick was intruded into both Huronian and Keewatin rocks. This dips southward at an angle of about 17°.

[1] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming, 3d ed.: Ontario Bur. Mines Rept., vol. 16, pt. 2, 1908; also 4th ed., vol. 19, pt. 2, 1913.

The deposits are short, narrow fissure veins, very numerous and rich. They are found in the Huronian, in the diabase, and in the Keewatin, but the more productive deposits are in the Huronian near the diabase sill, or they were below the footwall of the sill before the sill was eroded. The deposits are probably genetically related to the diabase intrusive, and the fractures have been assumed to represent cooling cracks formed in connection with the intrusion of the diabase. Postmineral fracturing and faulting have taken place extensively.

The principal sulphides of earlier age include smaltite, cobaltite, niccolite, chloanthite, bismuth sulphide, and dolomite, with some arsenopyrite and tetrahedrite. Pyrite, galena, and sphalerite are present in the wall rock near the vein. The silver occurs as native metal, proustite, pyrargyrite, dyscrasite, and argentite. The gangue minerals include calcite and quartz. Decomposition products are erythrite, annabergite, and asbolite.

The zone of oxidation is exceedingly shallow or altogether absent, but certain exceptionally rich superficial deposits, a few feet thick, are directly connected with the zone of weathering. This is called the "nugget horizon," and in it the smaltite and cobaltite have been largely altered to secondary minerals or leached out altogether. In this zone "cobalt bloom" and "nickel bloom" are characteristic minerals.

Extending downward 200 or 300 feet or more below the surface are rich silver minerals, largely in veinlets in earlier sulphides. The minerals of the veinlets include native silver, argentite, and calcite. The change from rich to low-grade ore is very abrupt, both in depth and on the strike. Van Hise[1] and Emmons[2] have attributed these richer silver ores to processes of sulphide enrichment, but Miller[3] is inclined to the belief that this feature of the genesis has been too much emphasized. He recognizes secondary ores in the district, but believes that rich ores, including those with native silver, have formed also through the agency of magmatic waters. He bases this conclusion on the fact that the rich parts of veins are said to be related to the diabase sill rather than to the present surface. He says: "Argentite, proustite, and native silver in hairlike crystals appear at times, judging from their mode of occurrence, to be of secondary origin." The fact that much of the native silver contains mercury is noteworthy.

[1] Van Hise, C. R., The ore deposits of the Cobalt district, Ontario: Canadian Min. Inst. Jour., vol. 10, pp. 45–53, 1907.

[2] Emmons, S. F., Cobalt district, Ontario, in Bain, H. F., and others, Types of ore deposits, San Francisco, pp. 140–156, 1911.

[3] Miller, W. G., Notes on the Cobalt area: Eng. and Min. Jour., vol. 92, pp. 645–649, 1911. Campbell, W., and Knight, C. W., Microscopic examination of the cobalt-nickel arsenides and silver deposits of Temiskaming: Econ. Geology, vol. 1, p. 767, 1906.

GOLD.

SOLUTION OF GOLD.

Although gold belongs to the same chemical family as copper and silver its activities differ in many respects from both these metals. It forms no insoluble compound in the oxidized zone and its sulphide is not precipitated by mineral waters. Unlike copper and silver it is insoluble in sulphuric acid. Wurtz[1] stated, in 1858, that ferric sulphate dissolves gold, and his statement has frequently been quoted in discussions of the processes of enrichment of gold deposits. It is, indeed, a common statement that ferric sulphate is the principal agent in the enrichment of gold deposits. Stokes[2] showed, however, that ferric sulphate will not dissolve gold at 200° C., except in the presence of a chloride, and its insolubility in ferric chloride and in ferric sulphate at ordinary temperatures has been verified by A. D. Brokaw.[3] W. J. McCaughey[4] found that gold is dissolved in a concentrated solution of hydrochloric acid and ferric sulphate and also in a concentrated solution of hydrochloric acid and cupric chloride, both experiments being carried on at temperatures from 38° to 43° C. Pearce,[5] Don,[6] and Rickard[7] performed experiments in which gold was dissolved in the presence of a chloride and manganese dioxide. Hydrochloric acid forms in the presence of sodium chloride and sulphuric acid, and in the presence of an oxidizing agent the hydrogen ion is removed to form water, leaving the chlorine in the so-called "nascent state." In this state it is in the uncombined or atomic condition and its attack is more vigorous. The reaction may be written:

$$MnO_2+2NaCl+3H_2SO_4 \rightarrow 2H_2O+2NaHSO_4+MnSO_4+2Cl.$$

At the beginning of the reaction manganese has a valence of 4; at the end a valence of 2. It is known that several oxides will release "nascent chlorine" at low temperature if the solutions are sufficiently concentrated, but in moderately dilute solutions manganese oxides

[1] Wurtz, Henry, Contributions to analytical chemistry: Am. Jour. Sci., 2d ser., vol. 26, p. 51, 1858.

[2] Stokes, H. N., Experiments on the solution, transportation, and deposition of copper, silver, and gold: Econ. Geology, vol. 1, p. 650, 1906.

[3] Brokaw, A. D., The solution of gold in the surface alterations of ore bodies: Jour. Geology, vol. 18, p. 322, 1910.

[4] McCaughey, W. J., The solvent effect of ferric and cupric salt solutions upon gold: Am. Chem. Soc. Jour., vol. 31, p. 1263, 1909.

[5] Pearce, Richard, Discussion of paper by T. A. Rickard on The origin of the gold-bearing quartz of the Bendigo Reefs, Australia: Am. Inst. Min. Eng. Trans., vol. 22, p. 739, 1894.

[6] Don, J. R., The genesis of certain auriferous lodes: Am. Inst. Min. Eng. Trans., vol. 27, p. 599, 1898.

[7] Rickard, T. A., The Enterprise mine, Rico, Colo.: Am. Inst. Min. Eng. Trans., vol. 26, pp. 978–979, 1897.

are probably the only common ones that are effective. Ferric chloride, ferric sulphate, and cupric salts are not more than a fraction of 1 per cent as effective as manganese salts and doubtless this fraction is exceedingly small.[1] Lead oxides are probably efficient, but they are rare in gold deposits.

A number of experiments on the solubility of gold in cold dilute solutions were made at my request by Mr. A. D. Brokaw.[2] The nature of these experiments is shown by the following statements, in which *a* and *b* represent duplicate tests:

(1) $Fe_2(SO_4)_3+H_2SO_4+Au$.
   (*a*) No weighable loss. (34 days.)
   (*b*) No weighable loss.

(2) $Fe_2(SO_4)_3+H_2SO_4+MnO_2+Au$.
   (*a*) No weighable loss. (34 days.)
   (*b*) 0.00017 gram loss.[3]

(3) $FeCl_3+HCl+Au$.
   (*a*) No weighable loss. (34 days.)
   (*b*) No weighable loss.

(4) $FeCl_3+HCl+MnO_2+Au$.
   (*a*) 0.01640 gram loss. Area of plate, 383 square millimeters. (34 days.)
   (*b*) 0.01502 gram loss. Area of plate, 348 square millimeters.

In each experiment the volume of the solution was 50 cubic centimeters. The solution was one-tenth normal with respect to ferric salt and to acid. In the second and fourth experiments 1 gram of powdered manganese dioxide also was added. The gold, assaying 0.999 fine, was rolled to a thickness of about 0.002 inch, cut into pieces of about 350 square millimeters area, and one piece, weighing about 0.15 gram, was used in each duplicate.

To approximate natural waters more closely, a solution was made one-tenth normal as to ferric sulphate and sulphuric acid and one-twenty-fifth normal as to sodium chloride. Then 1 gram of powdered manganese dioxide was added to 50 cubic centimeters of the solution, and the experiment was repeated. The time was 14 days.

(5) $Fe_2(SO_4)_3+H_2SO_4+NaCl+Au$.
   No weighable loss.

(6) $Fe_2(SO_4)_3+H_2SO_4+NaCl+MnO_2+Au$.
   Loss of gold, 0.00505 gram.

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[1] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, pp. 25–27, 1912.

[2] Brokaw, A. D., op. cit., pp. 321–326.

[3] This duplicate was found to contain a trace of Cl, which accounts for the loss.

The loss is comparable to that found in experiment 4, allowing for the shorter time and the greater dilution of the chloride.

Although the concentration of chlorine in most of these experiments is greater than that which is found in many mineral waters, it is noteworthy that solution of gold will take place with even a trace of chlorine (see experiment 2*b*), and without much doubt these reactions will go on also in the presence of only small quantities of manganese oxides.

SOURCES OF ACID IN GOLD DEPOSITS.

Gold can not be carried into solution under these conditions except in the presence of acid. If the solution is neutralized the gold is quickly precipitated. In sulphide ore deposits, as already shown (p. 91), acid is generated by the oxidation of sulphides, particularly by the oxidation of iron sulphides. The solution of gold is most important in the upper parts of the oxidized zones, where, in the presence of gold, pyrite is oxidized to ferric sulphate. The sulphuric acid which, under these conditions, is necessary for the reactions could easily be supplied, even above the zone where pyrite persists, by the leaching of basic iron sulphates, the formation of which tends to delay the downward migration of a part of the sulphuric acid that is released where ferric sulphate alters to limonite.

It is evident that the presence of an iron sulphide is an essential condition for the solution of gold. Ore bodies that do not contain pyrite or other iron minerals will show little evidence of transfer of gold, and in those that contain only a little pyrite the gold will not be carried far down, because the small amount of acid formed is quickly neutralized as it passes downward.

SOURCES OF CHLORINE IN GOLD DEPOSITS.

The sources of chlorine in ore deposits have been discussed elsewhere (p. 92), but, as it has been shown that chloride is the only natural solvent for gold in reactions causing superficial enrichment of gold deposits, the sources and distribution of chlorine are of special interest here. Other valuable metals are dissolved as sulphates with or without ferric ion but not gold, as has been shown. Chlorine has been found in all waters of gold mines where it has been sought. The amounts stated in analyses range from traces to 842.8 parts in a million. That a very small amount of chlorine is sufficient to dissolve gold in the presence of manganese is evident from experiment 2, above, where there is loss of gold through the introduction of a trace of chlorine without intent. Chlorine is carried by many sedimentary rocks and some minerals, such as apatite, scapolite, haüyne, and nosean, carry appreciable amounts. Salt cubes

are present in fluid inclusions in some vein quartz. In general, however, these sources of chlorine are unimportant. Its chief source is from finely divided salt or salt water from the sea and from other bodies of salt water. The salt is carried by the wind and precipitated with rain.[1] The amount of chlorine in natural waters varies with remarkable constancy with the distance from the shore; several determinations very near the seashore show from 10 to 30 parts of chlorine per million; a few miles away it is generally about 6 parts per million; 75 miles from shore it is generally less than 1 part per million. (See p. 93.)

The amount of chlorine contributed from this source even near the seashore appears small (from 6 to 10 parts per million), but it may be further concentrated in the solutions by evaporation or by reactions with silver, lead, and other metals, forming chlorides, which in the superficial zone may subsequently be changed to other compounds. In arid countries, as suggested by C. R. Keyes,[2] dust containing salt doubtless contributes chlorine to the mine waters. Penrose,[3] discussing the distribution of the chloride ores, pointed out long ago that these minerals form most abundantly in undrained areas.

SOURCES OF MANGANESE IN GOLD DEPOSITS.

It has been shown that the solution of gold depends on the presence of chlorine in the mineral waters, and the distribution of chlorine has been discussed briefly above. But chlorine is an efficient solvent of gold only when in the "nascent" state, and under natural conditions nascent chlorine is released principally by manganese oxides. The efficiency of other compounds that occur in gold deposits to release nascent chlorine is so small that they can probably be disregarded.[4] The sources and distribution of manganese are, therefore, important in connection with a study of the concentration of gold. The manganese minerals include the oxides (pyrolusite, psilomelane, manganite, manganosite, and pyrochroite); the sulphates (szmikite, mallardite, and apjohnite); the sulphides (alabandite and hauerite); the carbonates (rhodochrosite, manganiferous calcite, and manganiferous siderite); and the silicate (rhodonite). Besides these many rock-making silicates carry manganese. (See p. 437.)

[1] Jackson, D. D., The normal distribution of chlorine in the natural waters of New York and New England: U. S. Geol. Survey Water-Supply Paper 144, 1905.

[2] Keyes, C. R., Origin of certain bonanza ores in the arid region: Am. Inst. Min. Eng. Trans., vol. 42, p. 500, 1911.

[3] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 314, 1894.

[4] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, p. 25, 1912.

The commonest sources of manganese are probably the rock-making silicates of iron and magnesium, a little manganese being very commonly isomorphous with these elements. Manganese is more abundant in basic than in acidic rocks. The average of 1,155 determinations of igneous rocks[1] is 0.10 per cent manganese protoxide (MnO), though some contain more than 1 per cent.

Rhodonite is closely allied to the pyroxenes in crystallization, but, unlike them, it occurs as a gangue mineral in veins formed by ascending waters at moderate depths. It is found in ore of the Camp Bird, Tomboy, and other mines of the San Juan region, Colo., in the silver-bearing veins of Butte, Mont., at Philipsburg, Mont., and at many other places.

Rhodochrosite is more common in mines of the United States than rhodonite. It is present in many veins of the San Juan region, Colo., at Butte and Philipsburg, Mont., at Austin, Nev., and in many other western districts. Rhodonite is considered primary in practically all its occurrences and rhodochrosite is deposited in the main from ascending hot solutions also, but in some occurrences it has been regarded as a secondary deposit from cold solutions.

Manganiferous calcite, an isomorphous compound of rhodochrosite and calcite, is a source of abundant manganese in many later Tertiary deposits in Nevada, Montana, and Colorado. It is probably present in certain Mesozoic copper deposits of Shasta County, Cal., where, according to Graton,[2] wad occurs in the oxidized zone. Manganiferous siderite is abundant at Leadville, Colo., and according to Argall[3] it has supplied a large part of the manganese ore in that district.

Manganiferous ores of the precious metals are in general deposited at moderate depths. Consequently they are common in middle or late Tertiary deposits of western North America but very rare indeed in contact-metamorphic deposits, in the California gold veins, and in deposits formed at equal or greater depths.[4]

The sulphates of manganese are soluble and do not accumulate in veins to any important extent; all are secondary. The oxides and hydrous oxides, which are very numerous, are the products of weathering of all manganese compounds. None of them are known to be deposited by ascending hot waters except near the orifices of hot springs.

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[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 27, 1916.

[2] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 100, 1910.

[3] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, p. 282, 1914.

[4] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, pp. 47–49, 1912.

The sulphides of manganese are exceedingly rare. Alabandite has been found in the gold mines of Nagyag, in Transylvania; at Gersdorf, near Freiberg, Saxony; on Snake River, Summit County, Colo.; at Tombstone, Ariz., and at a few other places. Nishihara has shown, however,[1] that there are traces of a manganese sulphide, probably alabandite, in nearly all specimens of galena. Hauerite is a very rare mineral. I can find no record of its occurrence in the United States.

As to the amount of manganese required to accomplish appreciable enrichment of gold in its deposits, there are few data at hand. Doubtless only a little will permit some solution, but if ferrous sulphate is present gold will immediately be precipitated. Manganese dioxide, however, will convert ferrous sulphate at once to ferric sulphate, which does not precipitate gold. To convert the ferrous to ferric salt more manganese is required and appreciable amounts are necessary for the extensive downward migration of gold. In the deposits that show transportation of gold with which I am familiar manganese is conspicuously developed, particularly in the oxidized material. Its black or brown powder is easily recognized, as are the dendritic growths which some of it assumes.

PRECIPITATION OF GOLD.

The downward transportation of gold in chloride solutions obviously depends on the rate at which the solutions move downward, and the rate at which they react with ores and wall rock or with the reduced and neutralized solutions that have been shown (p. 149) to prevail in the deeper zones. The gold is precipitated from chloride solutions by ore and gangue minerals, by ferrous sulphate, by alkaline waters, and by hydrogen sulphide. Although gold sulphide is easily formed in the laboratory, it is noteworthy that this compound is unknown in nature. As shown by Brokaw[2] ferric sulphate converts the sulphide to native metal. The reaction is probably as follows:[3]

$$Au_2S_2+6Fe_2(SO_4)_3+8H_2O=2Au+12FeSO_4+8H_2SO_4.$$

As hydrogen sulphide does not accumulate in the superficial part of the zone of alteration and as other precipitates of gold are generally abundant it is probably of subordinate importance as a precipitant of gold.

[1] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals, and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, pp. 743–757, 1914.

[2] Brokaw, A. D., The secondary precipitation of gold in ore bodies: Jour. Geology, vol. 21, p. 254, 1913.

[3] Idem, p. 256.

The minerals that precipitate gold are legion. Copper, silver, mercury, and tellurium, all of which precede gold in the electromotive series (see p. 112), may displace it from gold-bearing solutions. Nearly all the sulphides of the metal[1] are fairly effective.

Brokaw[2] recently performed experiments precipitating gold, some of them earlier performed by Skey and Wilkinson. When gold chloride solution was in contact with sphalerite, after standing 24 days, the surface of the crystal was covered with shining flakes of gold. With pyrrhotite the action was more rapid, and the gold was precipitated in 3 days. The pyrrhotite was covered with a yellowish-brown coat, which was made up of minute crystals of gold partly embedded in material resembling limonite. A small fragment of a crystal of polybasite was placed in 5 cubic centimeters of gold chloride solution containing 0.5 per cent gold. After 10 days the gold had been completely precipitated, forming a dull coat over the crystal.[3] Palmer and Bastin[4] showed that galena, stibnite, copper-iron sulphides, and chalcocite will readily precipitate gold. Fused chalcocite is an exceedingly efficient precipitant of gold. According to Vautin[5] it will remove all the gold from a solution containing only 1 part in 5,000,000. The carbonates[6] also—calcite, siderite, and rhodochrosite—rapidly precipitate gold from the solutions in which it is held as chloride. Siderite is particularly efficient, probably because in acid abundant ferrous sulphate forms. Nepheline and leucite reduce acid solutions with great rapidity, as recently shown by Nishihara. Even comparatively stable minerals, like the feldspars and micas, give a distinctly alkaline reaction,[6] and, given time enough, an auriferous chloride solution would be neutralized, and gold would be precipitated by many minerals of the gangue and of the wall rock.

Where feldspar or rhyolite glass is attacked by sulphuric acid kaolin will form. Along with these changes, acidity is reduced, and the gold solution is neutralized. The association of rich gold ore

[1] Skey, W., On the reduction of certain metals from their solutions by metallic sulphides and the relation of this to the occurrence of such metals in their native state: New Zealand Inst. Trans. and Proc., vol. 3, 1871. Wilkinson, C., On the theory of the formation of gold nuggets by drift: Royal Soc. Victoria Trans. and Proc., vol. 8, 1867, pp. 11–15, 1867. Brokaw, A. D., The secondary precipitation of gold in ore bodies: Jour. Geology, vol. 21, p. 253, 1913. Palmer, Chase, and Bastin, E. S., Metallic minerals as precipitants of silver and gold: Econ. Geology, vol. 8, p. 140, 1913. Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 417, 1913.

[2] Brokaw, A. D., op. cit., p. 253.

[3] Idem, p. 256.

[4] Palmer, Chase, and Bastin, E. S., op. cit., p. 160.

[5] Vautin, Claude, The decomposition of auric chloride obtained in the chlorination of gold-bearing materials: Inst. Min. and Met. Trans., vol. 1, p. 274, 1893.

[6] Clarke, F. W., U. S. Geol. Survey Bull. 167, p. 156, 1900. Steiger, George, U. S. Geol. Survey Bull. 167, p. 159, 1900. Clarke, F. W., U. S. Geol. Survey Bull. 616, p. 480, 1916.

with kaolin at Bullfrog, Nev.,[1] particularly in the Montgomery Shoshone mine, and that in deposits at De Lamar, Idaho,[2] may have formed by some such reaction.

The minerals that precipitate gold as stated above include practically all the natural sulphides as well as the carbonates, many silicates, and organic matter. Among the common minerals, calcite, siderite, pyrrhotite, and chalcocite are noteworthy, however, for with these gold is precipitated very rapidly in zones of superficial

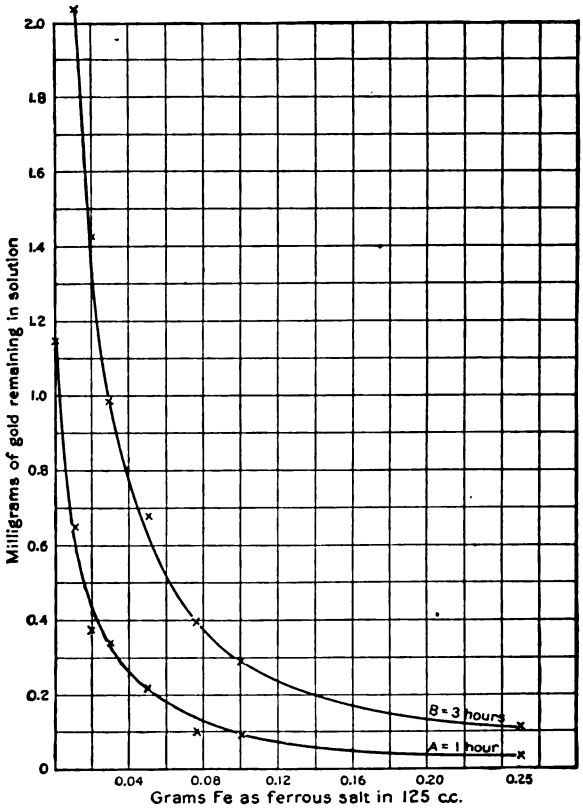

FIGURE 19.—Diagram illustrating the effect of ferrous sulphate in suppressing the solubility of gold in ferric sulphate solutions, where gold is dissolved as chloride. (Illustrating experiment by McCaughey.)

alteration. But any gold that may have been precipitated by these agents will be redissolved by chloride solutions in the presence of manganese oxides and ferric sulphate or sulphuric acid. It has been shown (p. 150) that ferric sulphate decreases and ferrous sulphate increases with increase of depth. Ferrous sulphate causes precipitation and inhibits solution of gold. Where it forms abundantly no gold is redissolved, and any in solution is reprecipitated.

[1] Ransome, F. L., Emmons, W. H., and Garrey, G. H., Geology and ore deposits of the Bullfrog district, Nevada: U. S. Geol. Survey Bull. 407, p. 104, 1910.

[2] Lindgren, Waldemar, The gold and silver veins of Silver City, De Lamar, and other mining districts in Idaho: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 171, 1900.

Experiments of McCaughey[1] show the effect of very small amounts of ferrous sulphate on solutions of gold in ferric sulphate. To a solution, 125 cubic centimeters, containing 1 gram of iron as ferric sulphate and 25 cubic centimeters of hydrochloric acid, ferrous sulphate was added in quantities containing from 0.01 to 0.25 gram of ferrous iron. The solutions were immersed in boiling water and subsequently 250 milligrams of gold was added. The dissolved gold was determined at the end of 1 hour and 3 hours. At the end of 3 hours the gold dissolved was greater, probably because some ferrous sulphate had changed to ferric sulphate. Even 0.01 gram of the ferrous iron greatly decreases the solubility of gold in the ferric sulphate and the solution of hydrochloric acid and 0.25 gram of ferrous sulphate drives nearly all the gold out of solution. These experiments are illustrated by figure 19, in which the horizontal lines represent ferrous salt put in the mixture and the vertical

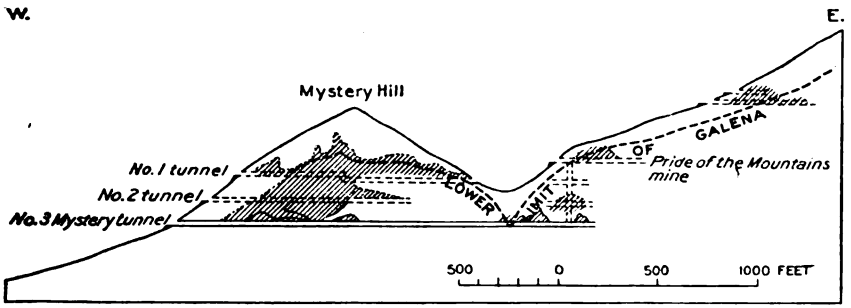

FIGURE 20.—Vertical longitudinal section of Mystery-Pride vein, Monte Cristo, Wash., showing shallow enrichment in pyrrhotite gold ore. After J. E. Spurr.

lines the amount of gold (in milligrams) dissolved by chlorine in the solution. The lower curve represents conditions at the end of 1 hour, the upper curve at the end of 3 hours, when some of the ferrous salt had oxidized by contact with the air.

An acid ferric sulphate solution reacting with pyrrhotite or siderite will readily form ferrous sulphate and the ferrous sulphate, as already stated, will precipitate gold and prevent its solution. Figure 20 is a longitudinal section of a pyrrhotite gold-bearing vein which has a shallow enriched zone. Calcite and other carbonates will decrease acidity of the solutions, and any deposit containing these minerals in abundance will carry only shallow secondary gold bonanzas, for in such deposits the gold can not migrate deeply. Nepheline and leucite also, as shown by Nishihara, are very effective. If inert minerals, like quartz and sericite, or minerals that act slowly, like pyrite, are present exclusively, gold will migrate to greater depths.

[1] McCaughey, W. J., The solvent effects of ferric and cupric salt solutions on gold: Am. Chem. Soc. Jour., vol. 31, pp. 1261–1270, 1909.

It is therefore evident that the depth to which gold will be carried by downward-moving waters in which it is held in solution depends not only on the permeability of the deposits but also upon the character of the ore and gangue minerals. If the gangue minerals precipitate gold rapidly it is not carried to great depths. If they reduce and neutralize the solution quickly no gold is redissolved. Secondary gold bonanzas are rare below the depths where such minerals prevail.

TRANSPORTATION OF GOLD AND DEPTHS TO WHICH IT MAY BE CARRIED.

The foregoing discussion of the conditions of the solution and precipitation of gold shows that it is carried downward in superficial alteration by stages. It is doubtless repeatedly dissolved and reprecipitated as weathering extends downward, and it will be fixed permanently only when it reaches an environment where the conditions become permanently reducing and alkaline. These conditions may exist in the zone of alteration above the water level, particularly where gold is associated with much calcite, siderite, or pyrrhotite, or where the deposits are in minutely fractured rocks containing olivine, nepheline, leucite, or other minerals that rapidly neutralize acid waters. (See p. 121.) At Creede, Colo.,[1] in the Amethyst vein, a fractured auriferous deposit containing mainly amethystine quartz, thuringite, barite, and pyrite, accompanied by galena, sphalerite, and chalcopyrite, some secondary gold has been carried downward to considerable depths. Rich bunches of ore consisting of the sulphides named, cut by stringers of gold-bearing manganese oxide, are found in this vein about 1,000 feet below the surface. Even in this deposit, however, where conditions appear to be favorable for the transportation of gold, the largest secondary gold deposits lie 200 to 700 feet below the surface in a zone where anglesite and cerusite are mingled with the manganese oxides and gold. At Philipsburg, Mont.,[2] the secondary ore in which gold is important is almost wholly in a zone between 200 and 800 feet deep, and in this the gold is concentrated in the upper part. At Bodie, Cal.,[3] the veins were not workable below a depth of 500 feet.

In a calcite gangue the secondary gold is deposited near the surface; at Marysville, Mont., according to Weed,[4] principally within 200 feet of the surface. At Cripple Creek, Colo.,[5] where the gold deposits carry a little manganese and are associated with nepheline

[1] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. — (in preparation).

[2] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 178, 1913.

[3] McLaughlin, R. P., Geology of the Bodie district, California: Min. and Sci. Press, vol. 94, p. 796, 1907.

[4] Weed, W. H., Gold mines of the Marysville district, Montana: U. S. Geol. Survey Bull. 213, p. 70, 1903.

[5] Lindgren, Waldemar, and Ransome, F. L., Geology and ore deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 167–168, 1906.

rocks, there is some evidence that gold has been dissolved and reprecipitated near the surface; but, as shown by Lindgren and Ransome, there has been little or no downward migration of gold. As long as alkali minerals, such as nepheline, are present to neutralize any acid formed by oxidation of pyrite, gold could not be dissolved, and any that may have been locally dissolved in an upper zone leached of alkalies would almost immediately be precipitated below. Here mass action due to the great abundance of precipitating agents would be most effective.

Several groups of calcitic gold veins have recently been described by Eddingfield,[1] Knopf,[2] and Ferguson.[3] The experimental work of Brokaw showed that calcite will rapidly precipitate gold from solutions in which it is dissolved in acid in the presence of chlorine and manganese. (See fig. 21.) It follows from this also that gold will not be dissolved in the presence of manganese and chlorine so long as calcite is effective. This was shown experimentally also by Eddingfield. Eddingfield states also that gold in deposits with calcitic gangue will not be transported, and he attributes the numerous rich stringers of gold and manganese in many Philippine deposits to the mechanical migration of gold. It is clearly unnecessary, however, to invoke mechanical migration, and it seems highly probable that iron and manganese oxide would be carried along mechanically by downward-moving waters quite as rapidly as gold and much more abundantly, and if so there would be little localization of gold. Since, as already stated, the calcite neutralizes or makes alkaline the acid gold-bearing solutions, as long as calcite is in contact with the solution gold will not be dissolved, but if any gold has gone in solution it will be precipitated. But the downward-moving acid, reacting on the calcite, uses it up and ultimately insulates passages through which acid solutions formed by oxidation of pyrite can move downward to greater depths, and they may carry gold downward until it comes into contact with fresh calcite. This is pointed

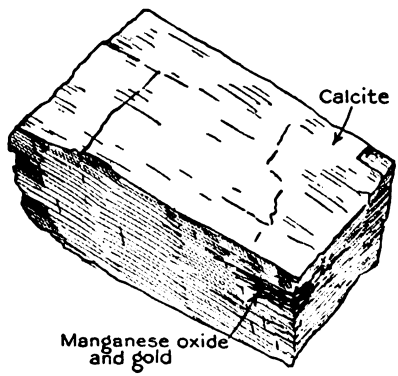

FIGURE 21.—Calcite that was immersed in a manganiferous acid gold solution. Gold and manganese have been precipitated together in cleavage cracks.

[1] Eddingfield, F. T., Alteration and enrichment in calcite-quartz-manganese gold deposits in the Philippine Islands: Philippine Jour. Sci., vol. 8, No. 2, sec. A, April, 1913.

[2] Knopf, Adolph, Ore deposits of the Helena mining region, Montana: U. S. Geol. Survey Bull. 527, p. 65, 1913.

[3] Ferguson, H. G., Gold lodes of the Weaverville quadrangle, California: U. S. Geol. Survey Bull. 540, p. 42, 1914.

out by Ferguson in the paper mentioned above, and by Bard,[1] in connection with a discussion of downward migration of copper in calcite gangue. Indeed, an experiment recorded by Eddingfield in the paper mentioned above illustrates this fact admirably. A solution of 10 per cent by weight sulphuric acid was allowed to percolate through a mixture containing 45 per cent powdered calcite. The filtrate was neutral to litmus after 48 hours and was still neutral to litmus after 72 hours, but after 75 hours it was acid. The solution had formed channels in the calcitic mass and was no longer reacting on the limestone, at least not rapidly enough to be neutralized. Briefly, in a gangue containing manganese with abundant calcite or other minerals that react rapidly with the acid waters, the solution of gold is delayed, but when the calcite or other active mineral has been dissolved and carried away, gold may then go into solution. It will be carried downward until it encounters ferrous sulphate, calcite, or some other precipitating material lower in the altering zone, when it will be deposited. In general calcite-rich veins are likely to carry any secondary gold bonanzas very near the surface, and the outcrops of such veins may be their richest parts. Siderite, nepheline, and pyrrhotite, as stated above, likewise neutralize acid solutions and precipitate gold very readily. Gold therefore descends tardily in deposits carrying appreciable amounts of these minerals.

PLACERS AND OUTCROPS.

Those deposits in which the transportation of gold is believed to have taken place are, probably without exception, manganiferous. Inasmuch as enrichment is produced by the downward migration of the gold instead of by its superficial removal and accumulation, it should follow that both gold placers and outcrops rich in gold would generally be found in connection with nonmanganiferous deposits; and this inference is confirmed by field observations. Placer deposits are in general associated with nonmanganiferous lodes, and such lodes are generally richer at the outcrops and in the oxidized zones than in depth, the enrichment being due, in the main, to a removal of the material associated with gold. Even under favorable conditions, however, gold is generally dissolved less readily and precipitated more readily than copper. Consequently its enriched ores are likely to be found nearer the surface.

As already stated, the rate of the transfer of gold from the surface downward depends on many factors, such as the fracturing of the deposit and its mineral composition. When erosion is rapid it overtakes solution and then auriferous outcrops or placer deposits may

[1] Bard, D. C., Absence of copper sulphide enrichment in calcite gangues: Econ. Geology, vol. 5, pp. 59–61, 1910.

be formed from manganiferous gold lodes. This is most likely when solution is slow, as it is where carbonates, particularly calcite and siderite, are abundant in the gangue, or where inclosing rocks contain nepheline, leucite, olivine, or other minerals that reduce acid solution rapidly. In a manganiferous calcite gangue gold may accumulate at the very outcrop, for the solutions could not long remain acid if passing through alkaline minerals. Some placer deposits are associated with gold lodes having a manganiferous calcite gangue. Examples of such deposits are found in the Philippine Islands and at Marysville, Mont. These are described by Eddingfield and by Knopf in the papers mentioned above.

CONCENTRATION IN THE OXIDIZED ZONE.

The concentration of gold in the oxidized zone near the surface, where the waters remove the valueless elements more rapidly than gold,[1] is an important process in lodes which do not contain manganese or in manganiferous lodes in areas where the waters do not contain appreciable chloride. In the oxidized zone in some mines it is difficult to distinguish the ore which has been enriched by this process from ore which has been enriched lower down by the solution and precipitation of gold and which, as a result of erosion, is now nearer the surface. It can not be denied that fine gold migrates downward in suspension, but this migration probably does not occur to an important extent in the deeper part of the oxidized zone. If the enrichment in gold is due simply to the removal of other constituents it is important to consider the volume relations and the mass relations before and after enrichment and to compare them with those now prevailing. It can be shown that the enriched ore in some lodes occupies about the same space that it occupied before oxidation. Let it be supposed that a pyritic gold ore has been altered to a limonite gold ore, and that gold has been neither removed nor added. Limonite (specific gravity 3.6 to 4), if it is pseudomorphic after pyrite (specific gravity 4.95 to 5.10) and if not more cellular, weighs about 75 per cent as much as the pyrite. In those specimens which I have broken cellular spaces occupy in general about 10 per cent of the volume of the pseudomorph. With no gold added, the secondary ore should not be more than twice as rich as the primary ore, even if a large factor is introduced to allow for silica and other gangue material removed and for cellular spaces developed.

Rich bunches of ore are much more common in the oxidized zones than in the primary zones of gold lodes. They are present in

[1] Rickard, T. A., The formation of bonanzas in the upper portions of gold veins: Am. Inst. Min. Eng. Trans., vol. 31, pp. 198–220, 1902.

some lodes which carry little or no manganese in the gangue and which below the water level show no deposition of gold by descending solutions. Some of them are doubtless residual pockets of rich ore that were richer than the main ore body when deposited as sulphides, but others are very probably ores to which gold has been added in the process of oxidation near the water table by the solution and precipitation of gold in the presence of the small amount of manganese contributed by the country rock. In view of the relations shown by chemical experiments it is probable that a very little manganese will accomplish the solution of gold, but it requires considerably more manganese to form appreciable amounts of the higher manganese compounds that delay the deposition of gold, suppressing its precipitation by ferrous sulphate. In the absence of larger amounts of the higher manganese compounds the gold would probably be precipitated almost as soon as the solutions encountered the zone where any considerable amount of pyrite or other reducing materials were exposed in the partly oxidized ore. From this it follows that deposits showing only traces of manganese, presumably supplied from the country rock, are not appreciably enriched by solution and downward migration, although they may show some solution and reprecipitation.

VERTICAL RELATION OF DEEP-SEATED ENRICHMENT IN GOLD TO CHALCOCITIZATION.

In several of the great copper districts of the West gold is a valuable by-product. In another group of deposits, mainly of Tertiary age and younger than the copper deposits, silver and gold are the principal metals, and copper, when present, is only a by-product. But in some of these precious-metal ores chalcocite is nevertheless one of the abundant metallic minerals and constitutes several per cent of the vein matter. In many ores it forms a coating over pyrite or other minerals. Some of this ore, appearing in general not far below the water table, is fractured spongy quartz coated with pulverulent chalcocite. A part of it contains a good deal of silver and more gold than the oxidized ore or the deeper-seated sulphide ore. Clearly the conditions that favor chalcocitization are favorable also to the precipitation of silver and gold.

The replacement of pyrite by chalcocite is, according to Stokes,[1] as follows:

$$5FeS_2+14CuSO_4+12H_2O=7Cu_2S+5FeSO_4+12H_2SO_4.$$

[1] Stokes, H. N., Experiments on the action of various solutions on pyrite and marcasite: Econ. Geology, vol. 2, p. 22, 1907.

This reaction is considered by Spencer[1] as comprising several stages, which may be indicated as follows:

$$2FeS_2+2CuSO_4=Cu_2S+2FeSO_4+S.$$
$$3S+2CuSO_4=Cu_2S+4SO_2.$$
$$6H_2O+5SO_2+2CuSO_4=Cu_2S+6H_2SO_4.$$

The reactions may differ as to details, but without any doubt ferrous sulphate is commonly present in zones where chalcocite is forming. The abundant ferrous sulphate must quickly drive the gold from solution. If the solutions that deposit secondary chalcocite are alkaline gold would quickly be precipitated. Hence it follows that there may be no appreciable enrichment of gold below the zone where chalcocitization is the prevailing process. Moreover, chalcocite will itself rapidly precipitate gold from acid solutions in which it is held as chloride. (See p. 311.) In deposits like disseminated chalcocite in porphyry, in which the chalcocite occurs in flat-lying zones related to the present topography, where the ore from which chalcocite was derived carried gold and where suitable solvents were provided, the gold, at least in the upper part of the chalcocite zone, should be rather evenly distributed and should increase and decrease in quantity with the chalcocite of the secondary ore. According to reports there is a fairly constant ratio between copper and gold in the disseminated deposits at Ely, Nev., and Bingham, Utah. In the copper deposits at Rio Tinto, Spain,[2] the secondary ores between the gossan and the primary sulphides carried high values in gold and silver. In view of the chemical relations it would appear that whatever gold and silver are present below a chalcocitized pyrite ore zone are, without doubt, primary.

Gold and silver are commonly associated in their deposits, and an exact knowledge of the solution and precipitation of the two metals in experiments where both are present would have great practical value. Although gold is dissolved in chloride solutions, silver chloride is but slightly soluble, and high concentration of the two metals could not exist in the same solution. There is so little exact information regarding the solubilities of gold chloride and silver chloride in solutions containing both metals that a discussion of their relations is little more than speculation, yet certain data should be considered in this connection. Silver chloride is slightly soluble in water, and silver may be held in small concentration in solutions in which gold also is dissolved. A mine water from the Comstock

[1] Spencer, A. C., Chalcocite deposition: Washington Acad. Sci. Jour., vol. 3, p. 73, 1913.
[2] Vogt, J. H. L., Problems in the geology of ore deposits, in Posepný, Franz, The genesis of ore deposits, p. 676, 1902.

oxidizing acid zone, with moderate supply of pyrite undergoing alteration, "autoreduction" would rarely take place, if ever, and there is excellent geologic as well as experimental evidence that gold is dissolved in the presence of manganese and acid.

Lehner states also that when a large excess of manganese chloride or sulphate is introduced into an open vessel with calcite and the solution greatly diluted to cause deposition to take place slowly, the calcite is after several days covered with a thick layer of manganese dioxide which contains only a very small amount of gold. When this experiment is repeated with a pure manganese solution and calcite, manganese dioxide is formed without gold in the same manner.

But this reaction, precipitating manganese dioxide without gold, could not go on at depths where air is excluded, for obviously there must be a source of oxygen to form an oxide in which manganese has a valence of 4 from manganous sulphate or chloride, in which the valence is 2. In many deposits gold is precipitated with manganese oxides below the zone where air is present. At such places no source of oxygen is apparent and probably no more manganese dioxide would form than would correspond to oxygen released by the gold solution. The so-called autoreduction of gold solutions can not be appreciably effective in the zone of solution as long as the solutions have moderately high acidity. It is true that in some deposits where gold and manganese have been precipitated together more manganese is present than gold. Why manganese is in excess has not yet been explained.

Possibly some of the manganese was precipitated on neutralization as hydroxide, which oxidizes almost immediately on being exposed to air, or perhaps as some other manganese compound that is soluble in acid but insoluble in alkaline solutions.

In some deposits there is evidence that gold has been dissolved and reprecipitated in the surficial zone, yet the secondary gold ore carries no manganese, or at least not more than a trace of manganese compounds. Such relations, according to Ransome,[1] are indicated by the gold veins of Farncomb Hill, in the Breckenridge district, Colorado, where in primary ores that carry manganese the secondary gold ore is almost free from manganese. It has been stated that gold may be precipitated from solutions in which it is dissolved as chloride either by the neutralization of the solution or by ferrous sulphate generated by the action of the solution on pyrite. Ferrous sulphate will precipitate gold, even from strongly acid solutions in which manganese would still remain in solution. It follows that manganese might not be precipitated with gold from acid chloride waters, even where manganese dioxide has supplied conditions for its solution, but

[1] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 170, 1911.

from neutralized solutions the gold and manganese could go down simultaneously. Gold is precipitated from chloride solution also by native metals, sulphides, organic matter, and many other materials. Experiments in the geological laboratory at the University of Minnesota show that many of these will precipitate gold with little or no manganese dioxide.

The size of the particles of gold has little value as a means of determining its origin. The gold deposited by the reduction or the neutralization of manganiferous compounds may be finely pulverulent or it may form nuggets of considerable size. Brokaw, in the experiments cited above, where gold and manganese were precipitated on calcite, obtained masses of gold distinctly visible without a hand lens.

In some deposits the purity or fineness of the gold may afford a means by which primary may be distinguished from secondary gold. In a deposit in northern Nevada the rich gold ore is electrum, a light-colored natural alloy of gold and silver. On this, deposited presumably from cold solutions, are small masses of dark-yellow gold which is apparently of great fineness. This criterion should be applied with caution, however, and the relations should be established independently for each particular deposit, for under some conditions doubtless secondary gold and silver are precipitated together.

GOLD AND SILVER TELLURIDES.

Petzite, sylvanite, krennerite, and calaverite are tellurides of gold and silver, the precious metals being present in varying proportions. All are primary. Hydrogen telluride (H_2Te) is made by the action of acids on metallic tellurides, but it decomposes readily even below 0° C. No clearly defined examples of secondary gold-silver tellurides are known to me.

SUMMARY.

Briefly stated, the chemical processes by which secondary deposits of gold are formed in nature are almost identical with those employed in barrel chlorination, a process that before the introduction of cyaniding was the chief wet method employed in recovering gold. The ore in the chlorination process is agitated with sulphuric acid, salt, and manganese dioxide; the gold solution is decanted or filtered off and treated with ferrous sulphate, which precipitates the gold. In nature the conditions that are favorable, if not essential, for gold enrichment are (1) chloride solutions, (2) iron sulphides, (3) manganese compounds. Where these conditions are supplied and where no very effective precipitant is at hand and erosion is not too rapid, gold placers are rarely formed, and outcrops of gold ores are likely

to be less rich than the ores that lie deeper. Where these conditions exist and where the lodes are fractured, gold will migrate downward. Many minerals will precipitate gold, but in the presence of some its precipitation is particularly rapid. These minerals include calcite, siderite, rhodochrosite, pyrrhotite, chalcocite, nepheline, olivine, leucite. In deposits that carry appreciable quantities of these minerals in ore or wall rock the downward migration of gold is delayed and gold bonanzas are likely to form at or very near the surface. Under these conditions, also, placers may form, even from manganiferous lodes. In a gangue of adularia, sericite, and quartz, with pyrite, chalcopyrite, galena, and sphalerite, gold may be carried downward several hundred or even a thousand feet, but this depth should be regarded as nearly the maximum and exceptional. As gold is so readily precipitated by many common minerals, it will generally migrate slowly in ground water.

GOLD-BEARING DEPOSITS.

APPALACHIAN DISTRICTS.

The gold deposits of the southern Appalachians are among the oldest gold deposits of the United States and were probably formed,[1] in the main, 3 or 4 miles below the surface at the time of deposition. Many of them are in mica schist and other crystalline rocks, and some are closely associated with granitic intrusions. Some are cut by diabasic intrusives, presumably later than the ore. The deposits have yielded considerable placer and lode gold. The minerals according to Graton,[2] include quartz, sericite, biotite, fluorite, gold, pyrite, galena, blende, pyrrhotite, chalcopyrite, and magnetite. Manganese minerals are not mentioned. In Becker's tabulation of the minerals of the gold mines of the southern Appalachians, compiled from all previous descriptions, and including some mines not described by Graton, pyrolusite is mentioned as occurring in only three mines and rhodochrosite in one.[3]

Few of these deposits have been extensively explored in depth, and data respecting the vertical distribution of the gold are therefore meager. Many of them are profitable near the surface, partly by reason of the rotten condition of the rock, which renders it more easily worked, and partly because gold is accumulated or enriched by the removal of valueless material. In general there is, according to Graton, very little evidence for or against the theory of the migration of gold; but such migration, if it has taken place, has been

[1] Lindgren, Waldemar, The gold deposits of Dahlonega, Ga.: U. S. Geol. Survey Bull. 293, p. 124, 1906.

[2] Graton, L. C., Reconnaissance of some gold and tin deposits of the southern Appalachians: Idem, p. 62.

[3] Becker, G. F., Reconnaissance of the gold fields of the southern Appalachians: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 3, p. 277, 1895.

extremely slow, for areas which have probably been exposed since Tertiary time show a marked concentration at and near the surface. Possibly some gold has been transferred to lower levels at the Haile mine, South Carolina, where, according to Graton, the limit of profitable mining is in general less than 200 feet below the limit of complete oxidation. In this zone scales of pyrite and free gold are found in joint cracks, indicating a relatively recent age. The deposits are cut by basic dikes. Prior to Graton's work many thought that the primary deposition of gold was genetically related to the dikes,[1] for the workable ore appears to be limited to the area cut by them. If the basic dikes (like most basic rocks) carry manganese, it would appear probable that gold had been dissolved and the ore enriched near the dikes.

Graton's tables show zinc blende in but one mine, the Kings Mountain mine, and pyrrhotite in but three others, the Haile, the Colossus, and the Asbury. Both minerals are in the ore of the Dahlonega district described by Lindgren.[2] All these deposits had relatively rich ore near the surface and in none of them did it extend to great depths.

Certain ore deposits of Alabama described by McCaskey[3] comprise fissure veins in granite and lenticular bodies in schists. The principal minerals are quartz, pyrite, and gold. Some garnet is found in the vein quartz at Pinetuckey. Weathering extends to water level, which lies 40 to 80 feet below the surface. The ores are oxidized above this level and are generally free milling, but below this level the ore is not profitably amalgamated so far as explored in depth. The ores are fairly regular in width and values, and no evidences of enrichment below the water level are recorded.

PORCUPINE, ONTARIO.

The Porcupine gold district,[4] which is in northern Ontario, on the Hudson Bay slope, about 100 miles northwest of Cobalt, was discovered in 1908 and is now assuming great importance. Its surface stands about 1,000 feet above the sea, is of low relief, and is wooded but not particularly swampy. It is covered thinly with clay, sand, and bowlder clay. The oldest rock series is the Keewatin, consisting of various volcanic rocks and their metamorphosed representatives. This series is more highly schistose here than at Cobalt. The prevailing rocks at Porcupine are basalts and other

[1] Maclaren, J. M., Gold, its geological occurrence and geographical distribution, pp. 57, 59. London, 1908.

[2] Lindgren, Waldemar, op. cit., p. 119.

[3] McCaskey, H. D., Notes on some gold deposits of Alabama: U. S. Geol. Survey Bull. 340, p. 36, 1908.

[4] Burrows, A. G., Ontario Bur. Mines Twentieth Ann. Rept., pt. 1, 1911. Hore, R. E., The nature of some Porcupine gold quarts deposits: Canadian Min. Inst. Jour., vol. 14, p. 171, 1911. Knight, C. W., Mineral associations at Porcupine: Min. and Sci. Press, vol. 102, p. 530, 1911.

green igneous rocks, which are cut by dikes and masses of quartz porphyry. Associated with the Keewatin also are sedimentary rocks, including iron formation (jaspilites), iron carbonate rocks, and limestone. Above the Keewatin lie Huronian rocks consisting of conglomerate, quartzite, and slate, altogether at least 400 feet thick. This series is tilted and locally rendered schistose. Granite (Laurentian) is intruded in the Keewatin; possibly granite is intruded also in the Huronian, but as granite pebbles are found in the Huronian, at least some of the granite is older than the Huronian. Diabase dikes are intruded in Keewatin and Huronian.

The ore deposits are veins and great irregular masses of schist seamed and impregnated with quartz and gold. Their outcrops are numerous and some of them are conspicuous, such as the Dome and West Dome, so called from their shape at the points of discovery. The deposits are in both Keewatin and Huronian rocks, and generally the lodes cut across the schistosity. The lodes range from horizontal to perpendicular. The domes on the Dome property were about 100 by 125 feet. The lodes show a strong tendency to parallelism. The Hollinger group strikes northeast; the Dome group nearly east. The gold is irregularly distributed, occurring along one or both walls, and some parts of the veins are high grade. Spectacular showings occur on many properties, but these are limited to parts of the veins. In view of the irregularity of the veins and the quantity of country rock mined the ore in general is considered low grade.

Besides quartz and pyrite the veins carry feldspar, tourmaline, and carbonates. The quartz of the Hollinger mine contains liquid and gas inclusions. Copper pyrites, galena, zinc blende, and pyrrhotite are found in some veins in very minor quantity. Locally the ore is fractured and cemented with quartz and pyrite. There is no evidence, however, of any secondary enrichment of gold by superficial reconcentration. These veins were probably formed at considerable depths and under high pressures, as is suggested by the presence of tourmaline and feldspar and gas inclusions in the quartz. Burrows believes that they are closely related to granitic intrusions. Near Night Hawk Lake are aplite dikes with fine veinlets of quartz from which a little gold has been obtained. W. G. Miller, in marginal notes on a map accompanying Burrows's report, states that specimens having the composition of granite are found in some of the veins that carry visible gold. Whether this granite is to be affiliated with the Laurentian mass that intrudes the Keewatin is uncertain. Some of the Laurentian granite is known to be older than the Huronian, which, as already stated, is the country rock of some of the veins.

BLACK HILLS, SOUTH DAKOTA.

The principal gold deposits of the Black Hills[1] are in pre-Cambrian schists which, like the ore bodies, are cut by Tertiary intrusives. Since the Cambrian conglomerates contain placer gold,[2] some of the ores must have been deposited in pre-Cambrian time. The most important deposits are comprised in the Homestake belt, about 3 miles long and 2,000 feet wide. The principal minerals are quartz, dolomite, calcite, pyrite, arsenopyrite, pyrrhotite,[3] and gold, with which are associated the minerals of the schist—quartz, orthoclase, hornblende, biotite, garnet, cummingtonite, actinolite, titanite, and graphite.[4] Pyrrhotite and arsenopyrite increase greatly with depth where pyrite decreases. The ores, though uniformly of low grade, are very profitable. Some of the ores at the surface were below the average tenor, while other surface ores were two or three times as rich as the average. The valuable minerals extend downward as far as exploration has gone and are fairly uniform to depths about 2,000 feet below the surface. In general, according to S. F. Emmons,[5] enrichment by surface leaching has relatively small importance.

MOTHER LODE DISTRICT, CALIFORNIA.

The Mother Lode district, California, as described by Ransome,[6] is an area of crystalline schists and altered igneous rocks with intruded granodiorite and related rocks. The deposits are fissure veins, which generally trend northwestward and at many places parallel the schistosity of the country rock. I have no record that the ores contain manganese minerals. Placers are abundantly developed, and at many places rich ore is found at the very surface. According to Ransome, there is no evidence that the mines grow suddenly richer at any particular depth, nor is there any recognizable regular change in the value of pay shoots with depth below the zone of superficial weathering. Some of these deposits are very regular and uniform in value and have been developed to very great depths.

NEVADA CITY AND GRASS VALLEY, CALIFORNIA.

The area of Nevada City and Grass Valley, Cal.,[7] includes metamorphosed Carboniferous sedimentary rocks, compressed into isoclines,

[1] Irving, J. D., Economic resources of the northern Black Hills: U. S. Geol. Survey Prof. Paper 26, 1904.

[2] Devereux, W. B., The occurrence of gold in the Potsdam formation, Black Hills, S. Dak.: Am. Inst. Min. Eng. Trans., vol. 10, p. 469, 1882.

[3] Sharwood, W. J., Analyses of some rocks and minerals from the Homestake mine, Lead, S. Dak.: Econ. Geology, vol. 6, pp. 729–789, 1911.

[4] Irving, J. D., op. cit., p. 90.

[5] Idem, p. 79.

[6] Ransome, F. L., U. S. Geol. Survey Geol. Atlas, Mother Lode district folio (No. 63), p. 3, 1900.

[7] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley districts, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, pp. 1–262, 1896.

and associated igneous rocks less intensely metamorphosed. Above these are slates with associated diabase and serpentine. These rocks are folded and metamorphosed, but are not so intensely compressed as the Carboniferous. Intruded into these rocks are great bodies of granodiorite, probably of early Cretaceous age. The ore deposits are strong fissure veins formed after the granodiorite intrusions. The minerals are quartz, chalcedony, magnetite, sericite, mariposite, pyrite, pyrrhotite, chalcopyrite, galena, blende, scheelite, arsenopyrite, tetrahedrite, stephanite, and cinnabar. Some earthy manganese ore occurs in small fissures in the granodiorite, but not in connection with the quartz veins.

Near the surface[1] the upper part of a vein is generally decomposed, forming a mass of limonite and quartz. The decomposition seldom extends more than 200 feet on the incline of a vein dipping 45°, or more than 150 feet below the surface. Fresh ore is found in places almost at the surface. The surface ore is generally richer than the fresh ore below, owing to the liberation of gold from the sulphides and the removal of substances other than gold. In this process silver also is partly removed. In some of the mines the lodes have been followed down the dip for 2,000 or even 3,000 feet. The unoxidized ore shows no gradual diminution of tenor in the pay shoots below the zone of surface decomposition. Within the same shoot there may be great variations of the tenor, but there is certainly no gradual decrease of it from the surface down. Important placer deposits were formed from these veins.

OPHIR, CALIFORNIA.

The rocks of the Ophir district, California,[2] comprise amphibolite schists and massive amphibolites, with intrusions of granodiorite. These rocks are cut by quartz veins which fill coordinate fissures. The minerals are gold, electrum, some iron, copper, and arsenical pyrites, with galena, zinc blende, tetrahedrite, and molybdenite. The gangue is mainly quartz, with a little calcite. The proportion of gold to silver varies by weight from 1:1 to 1:10, the gold predominating in value. Certain small ore shoots in veins in the amphibolite carry more than the usual tenor of gold, and the richest shoots are usually found where veins cross the belts rich in pyrite. According to Lindgren, such ore bodies may have been enriched by thermal waters concentrating gold from the pyrite in the iron belt. The common statement that the gold vein becomes barren as the depth from the surface increases is not justified, in his opinion,[3] by the

[1] Lindgren, Waldemar, op. cit., p. 182.

[2] Lindgren, Waldemar, The gold-silver veins of Ophir, Cal.: U. S. Geol. Survey Fourteenth Ann. Rept., pt. 2, p. 252, 1894.

[3] Idem, p. 279.

evidence afforded in the mines. The extensive development of placers, the value of the ore near the surface, and the occurrence of valuable ore shoots just below the surface are opposed to the notion of extensive migration of gold in these deposits.

SILVER PEAK, NEVADA.

According to Spurr,[1] the deposits of Silver Peak, Nev., are lenticular masses and fissure veins in Paleozoic sedimentary rocks. Genetically they are related very closely to granitic rocks which, as shown by Spurr, have alaskitic or pegmatitic phases. They are probably post-Jurassic, and should be grouped with the California gold veins, with which geologically they have much in common. Concerning the Drinkwater and Crowning Glory deposits, which are the most important examples, Spurr says that no decided enrichment of the ores by oxidation can be established. The ores in the upper tunnel seem to have been locally richer than any found in the lower tunnel, but this difference has no evident relation to the surface and is probably original. The gold occurs in finely disseminated particles and in auriferous sulphides. Placers are not mentioned.

EDGEMONT, NEVADA.

The gold deposits at Edgemont, Elko County, Nev.,[2] are in an area of quartzite, with intrusions of granodiorite. The deposits are fissure veins and their gold content is comparatively uniform. The ore consists of pyrite, galena, and arsenopyrite in a gangue of quartz. Copper carbonates and manganese minerals are rare or absent. The ore is stoped practically to the surface. There has probably been a slight amount of enrichment by removal of certain substances in the oxidized zone more rapidly than gold; there is no evidence that gold has been transferred below the water level by descending surface waters.

HEDLEY DISTRICT, BRITISH COLUMBIA.

The Hedley district, British Columbia, is in the valley of Similkameen River, some 30 miles north of the international boundary. The principal deposits are about 5,000 feet above sea level, and the whole district was covered with ice in the glacial epoch. The oldest rocks[3] are of Paleozoic age, probably Carboniferous, and consist of limestones, quartzites, and argillites, interbedded with which are subaqueous volcanic tuffs and breccias. These are intruded by

[1] Spurr, J. E., Ore deposits of the Silver Peak quadrangle, Nevada: U. S. Geol. Survey Prof. Paper 55, 1906.

[2] Emmons, W. H., A reconnaissance of some mining camps in Elko, Lander, and Eureka counties, Nev.: U. S. Geol. Survey Bull. 408, pp. 75–80, 1910.

[3] Camsell, Charles, The geology and ore deposits of Hedley mining district, British Columbia: Canada Geol. Survey Mem. 2, 1910.

Mesozoic diorite and gabbro, by Tertiary granodiorite, and by dikes of aplite, rhyolite, and andesite.

According to Camsell, the ore bodies are contact-metamorphic deposits, which occur mainly in limestone near intrusive diorite or gabbro. Metamorphism has been greatest along contacts with gabbro.[1] The sulphides carry abundant arsenopyrite, with pyrrhotite, chalcopyrite, pyrite, and zinc blende; the gangue minerals include garnet, epidote, tremolite, diopside, and axinite, with some calcite and quartz. No manganese gangue mineral is mentioned and but small amounts are shown in analyses of the igneous rocks.

There is a thin capping of iron oxide, which extends in general some 8 or 10 feet below the suface. Leaching is deeper in ores composed chiefly of pyrrhotite than in ores composed mainly of arsenopyrite. There is no zone of enriched sulphides; but gold, which is the principal metal, has been transported downward to some extent, according to Camsell, resulting in an enrichment near the surface and to depths perhaps several hundred feet below. In ore bodies having a low dip there is a notable concentration of gold along the gabbro footwall.

DOUGLAS ISLAND, ALASKA.

The gold belt of the Pacific coast extends from California northward into Oregon and Washington, and in large parts of these States its gold-bearing rocks probably lie beneath lavas. Farther north there are rocks nearly related to those of the California gold belt. The gold deposits of the Juneau belt,[2] as pointed out by Spencer, are probably similar in age and origin to the California veins. The Treadwell group of mines, on Douglas Island, exploits the most productive lode deposits in Alaska. Although the gold in the ore as mined runs only between $2 and $3 to the ton, the operations are highly profitable owing to low cost of mining and milling. On the mainland, across the narrow Gastineau Channel, a short distance from the Treadwell mines, the Alaska Gold Mining Co. has installed a large milling plant and plans to work a great low-grade deposit on a scale comparable to operations in the disseminated ("porphyry") copper deposits of the southwest.

The rocks of Douglas Island gold region consist of a series of Paleozoic greenstones, slates, and schists, intruded by altered gabbro. These rocks are changed by pressure and outcrop as parallel belts trending northwest. The dip is in general about 60° NE. The Paleozoic rocks are intruded by Cretaceous diorite and diorite porphyry.

[1] Camsell, Charles, op. cit., p. 25.

[2] Spencer, A. C., The Juneau gold belt, Alaska: U. S. Geol. Survey Bull. 287, 1906. Hershey, O. H., Geology of the Treadwell mine: Min. and Sci. Press, vol. 102, pp. 296–300, 334–335, 1911. Also in Bain, H. F., and others, Types of ore deposits, pp. 157–171, San Francisco, 1911.

At the Treadwell mines great dikes of albite diorite intrude the greenstones and schist, and the shattered diorite has been extensively replaced by mineralizing solutions and cemented by low-grade gold ore. Hydrothermal alteration is attended by the development of albite and calcite. The minerals include also quartz, rutile, mariposite, chlorite, epidote, siderite, pyrite, pyrrhotite, magnetite, chalcopyrite, and molybdenite. No manganese minerals are reported. The ore bodies, which, as already stated, are the albite diorite dikes, seamed and impregnated with pyrite, gold, and other minerals, are in places more than 200 feet wide and extend downward to great depths, 2,000 feet or more. According to Spencer, the ore shows no progressive change in appearance or value with increase of depth. In the lowest level it is quite as rich as in the upper workings. The best level of the Alaska Treadwell mine, according to Hershey, is 1,300 feet below sea level. Nothing in the character of the ore indicates any considerable concentration by oxidizing waters. The country has been recently glaciated and contains few gold placers. The gold accumulated at the apex since glacial time was, however, recovered by sluicing.

BERNERS BAY REGION, ALASKA.

The Berners Bay region lies along the Lynn Canal, 45 miles northwest of Juneau, Alaska. The country is an area of slates and graywackes of Jurassic or Cretaceous age and basic lavas and quartz diorites considerably altered by dynamic metamorphism. The Jualin diorite, intruding the sediments and lavas, is also later than the metamorphosed quartz diorite.[1]

The gold deposits, which are mainly in the Jualin diorite, are stockworks and fissure veins. The ores are composed of quartz, some calcite and pyrite, and minor amounts of chalcopyrite, galena, and sphalerite. The alteration of the wall rock was attended by the production of albite. Evidence of enrichment is lacking.

Knopf[2] says:

> Any enriched surface ores that may have existed within this region have been swept away by the powerful glacial erosion to which the region was subjected in the recent geologic past. The ores exposed at the surface are therefore of primary origin, modified to an unimportant extent by postglacial oxidation, and the outcrop of any ore deposit will furnish a true index of the value of the lode as a whole, depending on whether the distribution of values in the ore is or is not uniform.

GEORGETOWN QUADRANGLE, COLORADO.

The auriferous deposits of the Georgetown quadrangle, Colorado, are mainly at Idaho Springs and in the Empire district, although some are developed near Georgetown, in the area of the silver-lead

[1] Knopf, Adolph, Geology of the Berners Bay region, Alaska: U. S. Geol. Survey Bull. 446, 1911.

[2] Idem, p. 36.

deposits. As shown by Spurr and Garrey,[1] the gold lodes are probably of later age than the silver-lead deposits. They cut the crystalline schists and the Tertiary porphyries but are genetically related to alkali-rich intrusive rocks of middle or late Tertiary age. They carry pyrite, chalcopyrite, chalcocite, quartz, adularia, and gold and minor amounts of barite, fluorite, tellurides, and other minerals. Carbonates of iron, magnesium, lime, and manganese occur but are relatively rare. The deposits generally contain some galena and sphalerite. In many of the mines the ore averages 1 to 2 ounces of gold and 20 to 40 ounces of silver per ton. The lodes are usually oxidized at the surface and from 15 to 70 feet downward. They have yielded some moderately productive placers. In several mines the oxidized ore is much richer than the average ore. Below the zone of oxidation secondary chalcopyrite and chalcocite prevail for several hundred feet from the surface but decrease at greater depth. There is an important enrichment of gold and silver, coincident with the occurrence of the copper minerals. As stated by Spurr and Garrey[2]—

> In the mines mentioned a portion of the copper which has contributed to the enrichment of the original sulphides has been derived from the oxidized zone, but it seems unlikely that this has been the case with the gold and silver, which, like the enriched superficial portions of the argentiferous veins, must have been derived from the overlying portions of the lodes which are now eroded. * * *
>
> On the whole, the strongest evidence of the reworking of the ores by surface waters is afforded by markedly cupriferous ores. * * * Apart from this, however, and from the probable partial concentration of galena near the surface in some mines, the evidence of rearrangement of the ores by descending waters is in general not nearly so great as in the Georgetown district, and such reworking has probably taken place to a considerably less extent.

SAN JUAN REGION, COLORADO.

The gold deposits of the San Juan region, Colorado,[3] including those near Telluride, Silverton, and Ouray, are of varied character. They are mainly Tertiary, probably middle Tertiary, but have nevertheless undergone very extensive erosion. The region is moist, its altitude is 8,000 to 14,000 feet above sea level, and much of it has been glaciated. The prevailing rocks are volcanic tuffs, breccias, and flows and intrusive igneous rocks of intermediate or acidic composition.

In this elevated area the ground is frozen much of the year, and the rapid erosion is due largely to mechanical disintegration. Secu-

[1] Spurr, J. E., and Garrey, G. H., Economic geology of the Georgetown quadrangle, Colorado: U. S. Geol. Survey Prof. Paper 63, pp. 99–101, 1908.

[2] Idem, p. 149.

[3] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: U. S. Geol. Survey Bull. 182, 1901. Purington, C. W., Preliminary report on the mining industries of the Telluride quadrangle, Colorado: U. S. Geol. Survey Eighteenth Ann. Rept., pt. 3, p. 745, 1898. Purington, C. W., Woods, T. H., and Doveton, G. D., The Camp Bird mine, Ouray, Colo.: Am. Inst. Min. Eng. Trans., vol. 33, pp. 499–550, 1903.

lar decay or oxidation of the ores, according to Ransome, is not as a rule very extensive and is at some places negligible. Purington has pointed out, however, that the outcrops of the San Juan lodes are, in general, of lower grade than the ore a few feet below the surface, possibly by reason of the migration of gold in suspension. Many of the lodes are tight and do not appear to offer favorable conditions for downward migration of waters. The country is well drained and chlorine is probably not abundant in the mine waters. The conditions for deep-seated enrichment are therefore not particularly favorable, although some concentration has taken place locally by the leaching and removal of the less valuable materials from the ore. The workable ore appears to be mainly of primary origin.

At some places the gangue includes manganiferous minerals. There is evidence that gold was transported to a moderate extent. As Ransome points out,[1] black oxide of manganese occurs (in 1901) in the deepest workings in the Tomboy and Camp Bird mines and usually indicates good ore. These little sheets of rich, dark manganiferous ore, which fill postmineral fractures, Ransome regards as later than the general mass of the ore. It is reasonable to suppose that they represent deposition from solutions which dissolved gold in the upper portion of the lode, where ferric salts prevail, and which, in the presence of manganese, were able to transport their load to greater depths, but which, coming into contact with pyrite and other minerals, were ultimately reduced.

In the Yankee Girl mine, between Silverton and Ouray, the ores down to about 200 feet from the surface were mainly silver and lead, galena and pyrite being the principal minerals. The ore below this zone is composed mainly of stromeyerite, bornite, chalcocite, and some gray copper and barite, yielding about 30 per cent of copper and little or no lead. In depths below 600 or 700 feet the ore in this and adjoining mines is said to have gradually turned into a low-grade pyritous ore, which was of too low grade to work at a profit, so that the mines were closed. The ores in the copper-bearing zone had been exceptionally rich, carrying several thousand ounces of silver to the ton in carload lots.[2]

SUMMIT DISTRICT, COLORADO.

The Summit district is southwest of Alamosa, Colo., near the Rio Grande-Conejos county line. According to R. C. Hills,[3] the metal-bearing rocks are near the middle of the Tertiary eruptive series of south and southwest Colorado. The associated rocks are andesites,

[1] Ransome, F. L., op. cit., p. 101.

[2] Emmons, S. F., The secondary enrichment of ore deposits, in Pošepný, Franz, The genesis of ore deposits, pp. 451–452, 1902.

[3] Hills, R. C., Ore deposits of Summit district, Rio Grande County, Colo.: Colorado Sci. Soc. Proc., vol. 1, pp. 20–36, 1883.

trachytes, rhyolites, and other eruptives; but, unlike the eruptives of most Tertiary districts in this province, these rocks appear to have been closely compressed and form a series which, as shown in Hills's sketches, is probably isoclinal. Some features of the ore deposits are puzzling, but, whatever their genesis, they illustrate very clearly the theory of enrichment—a fact which was fully recognized by Hills as long ago as 1883.

The ore bodies, so far as exposed, are rudely tabular and approximately vertical. The ore is chiefly quartz and pyrite, but contains some enargite, galena, sphalerite, and other minerals.

Although Hills mentions brown oxides at several places, he does not say that they are manganiferous. Raymond[1] states that the oxides include those of purplish hue.

Placers appear to be of subordinate importance. The mineralized matter may be separated into three divisions—(1) the impoverished zone near the apex, (2) the zone of rich and partly oxidized ore, and (3) the zone of low-grade sulphides. The zone of impoverishment includes the outcrops of all but two of the lodes, and it extends downward to a depth of 50 feet or more. The zone of incompletely oxidized ore extends to a depth varying from a few feet to 300 feet. In this zone the quartz is colored dark brown by oxides, and the more highly auriferous material is characterized by an abundance of brown oxide. The gold in this ore carries only about 0.025 silver. According to Hills, all the bonanzas were confined to this zone. In some places gold appears in disseminated form, in innumerable small grains so aggregated as to resemble a continuous sheet of metal. Locally the grains unite and form flat nuggets 1 ounce or more in weight. According to Hills, the occurrence of this richer material is confined to the immediate vicinity of a central channel which has been filled with earthy matter, fragments of rock, and iron oxides. Some of the rich seams of gold powder have been introduced into fractures which cut barite. Below the rich and partly oxidized ore the primary sulphides appear to have been unworkable under conditions then existing. There is, however, in three mines a concentration of silver at greater depth than that of the gold bonanzas. Hills ascribes the two rich outcropping ore bodies, which are exceptional in this district, to intense kaolinization on either side of them, causing the country rock to be much more readily eroded than the extremely hard quartz. This consequently remained considerably above the general surface, forming a precipitous ridge that was, as he explains, protected from solution, which went on more vigorously below, in the places where snow and water accumulated.

[1] Raymond, R. W., Statistics of mines and mining in the States and Territories west of the Rocky Mountains, 1875, p. 329, 1877.

BOHEMIA DISTRICT, OREGON.

The Bohemia mining district of Oregon is an area of andesitic lavas and tuffs, which are cut by dacite porphyry and probably by basalt.[1] The deposits are fissure veins composed of sphalerite, pyrite, a little galena, and very little chalcopyrite, with a gangue of quartz, altered country rocks, and some calcite. According to MacDonald,[2]

> Some of the veins were brecciated after they were filled, and as a result oxygenated surface waters were able to percolate downward along the fractured zone. The ores were thus oxidized and sulphides leached out to depths of 100 to 300 feet, the depth depending on the degree of brecciation and the rate of erosion. The gold occurred as threads and filaments included in the pyrite. The pyrite was leached away, leaving the relatively insoluble gold and some iron oxide occupying a part of the small cavity left in the vein material. This process brought about an association of free gold with iron-stained spongy quartz and enriched the ore by leaching out the valueless sulphides. It also rendered the ore soft and porous, so that it is much more cheaply mined and milled than the unaltered ore.
>
> Small local enrichments of free gold occur at the junctions of fissures, pyrite being abundant at these junctions, as shown by the mass of iron oxide left. It is probable that the smaller particles of gold were dissolved from the upper parts of the vein * * * and were precipitated by the local masses of pyrite below.
>
> Some secondary sulphides were observed, but these are of no commercial value. They consist of pyrite crystals deposited in cracks in primary pyrite and of very small masses of sphalerite and galena. Other secondary minerals noted were calcite and, rarely, cerusite.

BULLFROG, NEVADA.

In the Bullfrog district, Nevada,[3] the principal deposits are fissure veins in rhyolite. The minerals include pyrite, quartz, and manganiferous calcite. Enough manganese is present in the calcite to stain much of the oxidized ore chocolate-brown or black. No placers are developed. The outcrops were comparatively poor, but good ore was encountered within a few feet of the surface, and some of the deposits were worked by open cut. Some of the ore deposits decrease in value below the 400-foot level, where ore carrying less than $5 a ton is encountered. Since the ore above this level carried many times this value, it appears that there has been a secondary concentration by surface waters and that the rich ore is related to the present topographic surface.

In these ores, as in other manganiferous gold ores in calcite gangue, secondary deposition of gold has not been carried far below the surface.

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[1] Diller, J. S., The Bohemia mining region of western Oregon: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, pp. 7–64, 1900. MacDonald, D. F., Notes on the Bohemia mining district, Oregon: U. S. Geol. Survey Bull. 380, p. 80, 1909.

[2] MacDonald, D. F., op. cit., p. 82.

[3] Ransome, F. L., Emmons, W. H., and Garrey, G. H., Geology and ore deposits of the Bullfrog district, Nevada: U. S. Geol. Survey Bull. 407, 1910.

GOLD CIRCLE, NEVADA.

The deposits of the Midas or Gold Circle district, Nevada,[1] are in late Tertiary rhyolites. The lodes are replacement veins and sheeted zones and carry considerably more gold than silver by value. In the oxidized zone some of the ore is rich, but the sulphides are comparatively regular in value and give no evidence of extensive enrichment. Some oxidized ore shoots appear to have been increased in value by the removal of substances more soluble than gold. The minerals are chiefly quartz and pyrite. The oxidized zone contains seams of very rich gold ore, composed of manganese, limonite, kaolin, and soft hydrous silica.

DELAMAR MINE, NEVADA.

The Delamar mine, in southeast Nevada, is in quartzite which is cut by acidic porphyry dikes. The ore body, described by S. F. Emmons,[2] is related to a strong zone of fracturing, which strikes with the quartzite but dips about 75°, or nearly at right angles to the dip of the quartzite. The ore is in shoots or zones of crushed quartzite. The chief ore body, which is, roughly speaking, a long and comparatively thin, nearly upright cylinder, is divided into four parts by a dike of quartz porphyry and a more basic dike, which cross nearly at right angles in the ore body. The ore follows the line of intersection of the two dikes rather closely. The ore at the bottom of the mine consists of quartz and pyrite, which fill fractures in the altered quartzite. Where the dikes cross in the ore body the light-colored dike appears to be continuous, but notwithstanding this the line of the dark dike across the light one is generally marked by a slight stain of manganese dioxide, which, as stated by Emmons, is characteristic of the "black" dike and perhaps gives it that name.

Oxidation extends as far down as the tenth level. The ore that has been found below that level is too low in grade to pay for mining. The gold ore carries silver and some copper. The tenor in gold increased from the surface downward to about the seventh level, although the values were not evenly distributed. Some lots of ore ran as high as 30 ounces per ton, and the richer parts of the mine averaged from $30 to $70 per ton. At the tenth level they had decreased to $4 or $5 per ton.

WEAVERVILLE QUADRANGLE, CALIFORNIA.

The Weaverville quadrangle is in the Klamath Mountains, northern California, and includes parts of Trinity and Shasta counties.[3]

[1] Emmons, W. H., A reconnaissance of some mining camps in Elko, Lander, and Eureka counties, Nev.: U. S. Geol. Survey Bull. 408, pp. 48–57, 1910.

[2] Emmons, S. F., The Delamar and the Horn Silver mines: Am. Inst. Min. Eng. Trans., vol. 31, pp. 658–675, 1901.

[3] Diller, J. S., Auriferous gravels in the Weaverville quadrangle, California: U. S. Geol. Survey Bull. 540, pp. 11–21, 1914. Hershey, O. H., Gold-bearing lodes in California: Am. Geologist, vol. 25, pp. 76–96, 1900. MacDonald, D. F., Notes on the gold lodes of the Carrville district, Trinity County, Cal.: U. S. Geol. Survey Bull. 530, pp. 9–41, 1913.

It is an area of schists and Paleozoic and Mesozoic sediments and igneous rocks, complexly folded and faulted, which was intruded by soda granite and granodiorite and possibly by other rocks, as well as by many dikes having a wide range in composition.[1]

Near the east border of the quadrangle is the area that contains the copper deposits of Shasta County, the geology of which is discussed on page 234.

The principal deposits of the quadrangle are fissure veins, generally narrow and steep, and small, rich bodies of gold ore known as "pockets." The fissure veins are of the "California type" and resemble the lodes of the Sierra Nevada. They carry quartz, calcite, mica, some albite and tourmaline, pyrite, arsenopyrite, chalcopyrite, and a little galena and sphalerite. According to Ferguson,[2] manganese oxide is not a prominent feature of the veins of this type, though in some the oxidized ore carries rich pockets marked by black powdery manganese.

Of very great interest in this region are the rich "pocket" mines. In these practically all the gold is contained in small scattered masses near the surface, all of them being found at or near the contact of black slate with some other formation, generally meta-andesite.[3]

The chief gangue minerals of the pocket deposits are manganiferous calcite and some quartz, which is said to be also manganiferous. According to Ferguson, the gold was dissolved through the agency of manganese and precipitated mainly by the organic matter of the black slate. Some gold is found also in cleavage planes of calcite, indicating probably a precipitation by neutralizing an acid gold-bearing solution.

In the Mad Mule mine[4] the ore lies close to a diorite porphyry dike, which cuts meta-andesite, alaskite, slate, and conglomerate. The rocks are cut by many small veinlets, but the chief concentrations are near the contact of slate and porphyry. The ore mined is mostly calcite, which occurs at intervals along both hanging wall and footwall in small lenses known as "points." These points have a variety of forms. The common form is a flat lens of calcite, generally not over 4 inches thick, deposited in the trough formed by some irregularity in the contact of the dike and slates.[5] The calcite lenses are as a rule not more than 3 or 4 feet in length along the strike and have been followed upward for as much as 20 or 30 feet. Gold, which is mined only in the "points," commonly forms thin

[1] Diller, J. S., op. cit., p. 13.
[2] Ferguson, H. G., Gold lodes of the Weaverville quadrangle, California: U. S. Geol. Survey Bull. 540, pp. 22–79, 1914.
[3] Idem, p. 40.
[4] Idem, p. 52.
[5] Idem, p. 53.

films on the surfaces of the calcite at the junction with the slate, rarely becoming plates of noticeable thickness. It is said that a plate of gold taken from the mine was nearly a quarter of an inch thick and weighed over 100 ounces. Gold also occurs in much smaller masses entirely within the calcite, here following the cleavage planes. Invariably it is close to the slate or not more than half an inch distant. The intersection of manganese-bearing quartz stringers with the calcite of the above "points" is regarded as an indication of a rich pocket.[1]

The pockets all lie near the surface and at some places gold was recovered by sluicing; apparently they play out at shallow depths. It is noteworthy that the conditions here are evidently favorable for the solution of gold, but, owing to the presence of carbonaceous shale and abundant calcite, conditions are exceptionally favorable for its reduction and precipitation; consequently the richer bodies of gold ore have not migrated to any great depth but have remained at or near the surface.

EXPOSED TREASURE MINE, CALIFORNIA.

The Exposed Treasure mine,[2] near Mohave, Cal., has produced considerable gold and silver. It is in an area of granitic rocks cut by quartz porphyry and capped by rhyolite. The lodes are probably Tertiary. The Exposed Treasure vein dips about 45° E. and is a sheeted brecciated zone. Considerable fissuring has taken place since the ore was deposited.

The lodes are continuous and many of them are of great width, some being 40 feet and more from wall to wall, but the pay streaks, from 4 to 15 feet in width, lie in well-defined shoots and overlapping shoots or lenses. Shoots or lenses which now reach the surface contained important quantities of calcite and manganese dioxide.

The oxidized ores contain much manganese dioxide, the concentrates carrying 12 per cent. In the altered oxidized ore are kernels of ore containing pyrite, chalcopyrite, galena, and sphalerite, and these are richer in the precious metals than the altered friable ore. As observed by De Kalb,

> The altered ore bore manifest signs of extensive leaching, and where it had become almost completely decolorized by the removal of iron the precious-metal contents had nearly disappeared, and such ore never contained copper except in the form of chrysocolla.
>
> The absence of sulphides in all the [oxidized] ores, except in the cherty skeletons and in the undecomposed kernels of hard ore, was very complete. The mill concentrates (150 into 1) had an average composition of SiO_2, 30; FeO,

[1] Ferguson, H. G., op. cit., p. 54.

[2] De Kalb, Courtenay, Geology of the Exposed Treasure lode, Mojave, Cal.: Am. Inst. Min. Eng. Trans., vol. 38, pp. 310–319, 1908.

37; * * * and MnO_2, 12 per cent. These concentrates never contained more than 1.5 per cent of sulphur. * * *

In the lower friable siliceous ores the ratio of gold to silver was as 1 to 12, while in the upper mangano-calcitic ores the ratio was as 1 to 72. Assays of gold scale and of coarse gold panned out from all parts of the mine showed a remarkably uniform alloy of 1 part of gold to 0.461 part of silver. The silver in the upper portion of the mine was present almost wholly in the form of silver chloride.

On the assumption, from the evidence, that the abundance of chlorides would prevent the leaching out of silver and its reconcentration below water level, and that the ferric and cupric sulphates would have abstracted large quantities of the gold, which would be redeposited lower down, together with the copper in the form of secondary enrichments, it was natural to predict an ore below permanent water rich in these metals and relatively lean in silver. It would be difficult to conceive a nicer justification of theory than that which was afforded when development at length extended below water level. The ore consisted of a hard bluish-gray mass of original chert-cemented breccia, recemented by quartz, with partial replacement of the granite and quartz porphyry by silica, heavily impregnated with sulphides, among which were considerable quantities of chalcopyrite, some bornite, and some covellite. The gold content of the ore had increased 150 per cent above the average in the friable siliceous ores on the upper levels, and the ratio of the gold to silver was as 1 to 2.

BODIE, CALIFORNIA.

The deposits of Bodie, Cal., are east of the Sierra, near the State line. They are not of the California type but are associated with andesite and belong to the late Tertiary group so extensively developed in Nevada. R. P. McLaughlin[1] has described the most important mines. The lodes are fissure veins in andesite. Nearly all strike northward and are approximately parallel. The ore carries about equal amounts of gold and silver. The deposits are developed extensively to a depth of 500 feet below the surface. One shaft is 1,000 feet, another 1,200 feet deep. Outcrops of encouraging value are rare. Almost without exception the veins have failed to carry pay ore beyond 500 feet below the surface, but above this depth occur large, rich ore bodies, which, according to McLaughlin, carry ore worth as much as $400 a ton. Faulting and displacement are probably of later date than the period of vein formation. Some of the oxidized ore carries manganese dioxide. It is "loose and clayey in texture and carries some silver to the exclusion of gold."

MANHATTAN, NEVADA.

The gold deposits at Manhattan, Nev., although inclosed in schists, are in an area of Tertiary volcanic activity and should be classed with the deposits formed in Tertiary time. Although the schists contain stringers of gold of uncertain genesis, the principal deposits

[1] McLaughlin, R. P., Geology of the Bodie district, California: Min. and Sci. Press, vol. 94, p. 796, 1907.

are steeply dipping lodes of quartz and calcite, stained with iron and manganese oxides. Some placers are developed. Rich ore was found very near the surface, but it was richer a few feet below the outcrop than at the surface. Some fracturing has taken place since the deposits were formed. The gold of many of the pockets of rich ore is intimately associated with iron and manganese oxides.[1] In view of the fact that the unaltered sulphides had not been encountered when the mines were visited, the character of the primary ore is unknown to me, nor is it certain that all the deposits have decreased in value below the oxidized zone.

LITTLE BURRO MOUNTAINS, NEW MEXICO.

The Little Burro Mountains, just north of Tyrone, N. Mex., consist of pre-Cambrian granitic rocks overlain by Cretaceous sediments and later eruptive rocks. These are partly buried by Tertiary (?) lavas and intruded by rhyolitic or trachytic stocks.[2] Some gold veins in this region carry abundant manganese dioxide and chlorides. The ore minerals include chalcopyrite, pyrite, sphalerite, and galena.[3] Zinc blende is conspicuous, and the ores assay 10.2 per cent zinc.

According to Paige,[3]

> The Wyman vein has been worked over a distance of about 500 feet and not below a depth of 110 feet. The richest returns came from the part above a depth of 40 feet. Silver chloride and gold furnished the values in these upper levels. Zinc and copper are reported to have increased as greater depth was attained and gold and silver to have fallen to $3 to $5 a ton. In the upper portion of the vein much of the ore is reported to have assayed $200 to the ton.

ANNIE LAURIE MINE, UTAH.

The Annie Laurie mine,[4] 175 miles south of Salt Lake, Utah, is in an area of dacite, rhyolite, and rhyolite tuff and probably belongs to the later Tertiary group. The vein is poorly exposed at the surface, being largely covered by morainal material. Lindgren says:

> The quartz forms an almost continuous sheet along the vein, rarely less than 3 feet in thickness and often expanding to a width of 20 feet or more. As a rule, the walls are poorly defined and slickensides indicating motion are rare. In places it contains, parallel to the walls, streaks of iron oxides and black, sooty manganese ores. * * *
>
> The mine workings have not penetrated below the zone of oxidation, and neither the quartz nor the country rock seems to contain any unoxidized sulphides.

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[1] Emmons, W. H., and Garrey, G. H., Notes on the Manhattan district: U. S. Geol. Survey Bull. 303, pp. 87–90, 1907.

[2] Paige, Sidney, Metalliferous ore deposits near the Burro Mountains, Grant County, N. Mex.: U. S. Geol. Survey Bull. 470, p. 132, 1911.

[3] Idem, p. 136.

[4] Lindgren, Waldemar, The Annie Laurie mine, Piute County, Utah: U. S. Geol. Survey Bull. 285, pp. 87–90, 1906.

In the absence of extensive postmineral fracturing one would suppose that the conditions for migration of gold were not particularly favorable. Since the workings had not penetrated sulphide ore at the date of Lindgren's report, direct evidence was lacking.

MARYSVILLE, MONTANA.

Marysville, Mont., about 18 miles northwest of Helena, is in an area of pre-Cambrian sandstones, shales, and limestones that are intruded by quartz diorite and by later porphyry dikes.[1] The deposits are mainly in fault fissures in sedimentary rocks. Placers are developed. The Drumlummon mine has been developed for about 3,000 feet horizontally and to a depth of 1,600 feet, but no ore was found below the 1,000-foot level.

According to Weed,[2]

> In general, it may be said that all the veins of the district carry rich ores in bonanzas and ore shoots within the first 200 feet from the surface, but that in depth the ores rapidly decrease in value until the vein is no longer workable. It may also be said that the ore shoots were well defined and the intervening vein matter barren and unworkable. The pitch of the ore shoots conforms to the usual habit, dipping to the right when looking down the dip of the vein. The ores consist of sulphides and sulphantimonides of silver, with gold aggregating 60 per cent of the total value. In the upper levels the ore is somewhat oxidized and in the ore shoots of the Drumlummon mine carried extremely high values.

The gangue in depth is highly calcitic, and the rich ores of native gold that are found at and near the surface are associated with abundant manganese oxides.

GIBBONSVILLE, IDAHO.

The Gibbonsville district,[3] in Lemhi County, Idaho, is an area of pre-Cambrian quartzites and slates, intruded by diorite and capped by andesite. Numerous faults, both normal and reverse, parallel to the bedding, cross the veins at many places. The ore minerals are quartz, some calcite, pyrite, and a little chalcopyrite. The water level is high and the limit of strong oxidation in few places exceeds 150 feet and in many is less.

The ore occurs in shoots which pitch eastward with the dip of the country rock. Their distribution seems to bear a definite relation to the kind of inclosing rock; a vein crossing the several types of rock is commonly barren in the diorite, poor in the quartzite, and

[1] Barrell, Joseph, Geology of the Marysville mining district, Montana: U. S. Geol. Survey Prof. Paper 57, 1907. Knopf, Adolph, Ore deposits of the Helena mining region, Montana: U. S. Geol. Survey Bull. 527, pp. 62–65, 1913.

[2] Weed, W. H., Gold mines of the Marysville district, Montana: U. S. Geol. Survey Bull. 213, p. 70, 1903.

[3] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, pp. 80, 131, 1913.

productive in the black clay slate. Within the shoots there is a secondary concentration whereby a leached zone of 15 to 30 feet is found at the surface, followed by a zone of enriched ore extending usually about 100 feet deep, where it grades into the unaltered deposit.

Manganese occurs as conspicuous stains in the oxidized ore, and the barren zone near the surface is probably due to leaching. According to Umpleby, however, the heavy gold particles may settle downward in the loose oxidized material. Residual concentration, due to the removal of other constituents, may account for part of the enrichment of gold in the oxidized zone, but the gold has probably been leached out near the surface and precipitated below.[1]

MONTE CRISTO, WASHINGTON.

Monte Cristo stands high on the west slope of the Cascade Range about 40 miles east of Everett, Wash., in a rugged region where the climate is moist and erosion is rapid. Here Eocene arkosic sediments are overlain by andesites, and cut by intrusive masses and dikes of dioritic rocks. The deposits include fissure veins, sheeted zones, and mineralized joints. The most valuable deposits are on the Mystery-Pride vein.

The chief ores in the Monte Cristo district consist of pyrite, pyrrhotite, arsenopyrite, zinc blende, galena, and chalcopyrite. Realgar is a common alteration product from arsenopyrite. Among the rarer minerals are chalcocite, bornite, molybdenite, and stibnite. Metallic arsenic is said to have been found on Goat Lake not far northeast of Monte Cristo. Among the oxidation products of the sulphides are malachite, limonite, hematite, melaconite, and scorodite.[2]

The ground-water level almost coincides with the surface. Except along openings thorough oxidation rarely extends deeper than 10 feet. The ore near the surface and for depths generally extending down 100 to 150 feet is chiefly galena but includes some zinc blende and chalcopyrite, with about an ounce of gold and 12 ounces of silver to the ton. In places it is much richer. The gangue minerals are quartz and calcite. Below this depth the ores are arsenopyrite, pyrite, pyrrhotite, zinc blende, and chalcopyrite, with very little lead and about half as much of the precious metals. The deeper ore is cut by veinlets of realgar, stibnite, and molybdenite, all of which are regarded by Spurr as secondary. The rich sulphide zone clearly conforms to the present surface, formed in late Pliocene or early Pleistocene time, and was presumably deposited by descending waters.

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[1] Umpleby, J. B., op. cit., p. 61.

[2] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 803, 1901.

PHILIPPINE DISTRICTS.

In the Baguio district, Philippine Islands,[1] the gold deposits are fissure veins in andesite near the contact of andesite and sandstone or shale. The filling is quartz, pyrite, gold, calcite, and manganese, the manganese presumably in calcite. At many places the gold is highly concentrated in the upper parts of the veins, extending in some deposits to the very surface.

In the Aroroy[2] district the deposits are similar and are likewise in andesite. Enrichment is marked in the upper workings and along manganese streaks. In the Suyoc district manganese is practically unknown. No enrichment is reported. These veins have supplied valuable placers.

Eddingfield,[3] in discussing the distribution of lode ores and placers in the Philippines, notes some placer deposits that have apparently been derived from manganiferous calcitic lodes. In general the size and richness of these appears to be as yet uncertain. The Lepanto placer, however, is large and carries 20 cents to the cubic yard. But the gold in this placer is said to have been derived from the veins of the Suyoc district, in which manganese is very subordinate, having been noticed by Eddingfield[4] in only one vein. However, valuable placer deposits under some conditions may form from manganiferous calcitic ores. Examples have already been noted.

MOUNT MORGAN MINE, QUEENSLAND.

The Mount Morgan mine[5] is about 25 miles southwest of Rockhampton, Queensland. The country is tropical and the "mount," which is only 500 feet above Dee River, is 1,225 feet above sea level. It is one of the most productive gold mines in the world, having yielded more than $60,000,000 before 1907. To the end of 1907 it had paid in dividends about $35,000,000. Recently several million tons of copper-gold ore have been developed.

The country is an area of sedimentary and igneous rocks, the oldest sediments belonging to the Gympie formation (Carboniferous), which consists of quartzite, slates, graywackes, schists, and limestones. Remnants of the Desert sandstone (Upper Cretaceous) also are found here and there. Near the ore deposits there are large

[1] Eddingfield, F. T., Ore deposits of the Philippine Islands: Philippine Jour. Sci., vol. 8, No. 2, sec. A, pp. 81–105, 1913.

[2] Ferguson, H. G., The gold deposits of the Philippine Islands: Econ. Geology, vol. 6, p. 126, 1911.

[3] Edingfield, F. T., op. cit., p. 103.

[4] Idem, p. 96.

[5] Rickard, T. A., Am. Inst. Min. Eng. Trans., vol. 20, p. 133, 1891. Jack, R. L., Queensland Geol. Survey Rept. No. 132, 1898. Wilson, J. B., Mount Morgan ore deposits, Queensland: Inst. Min. and Metal. Trans., vol. 20, p. 89, 1911. Clark, Donald, Australian mining and metallurgy, p. 267, Melbourne, 1904. Maclaren, Malcolm, Gold, its geological occurrence and geographic distribution, p. 333, London, 1908.

bodies of granitic rocks, consisting of granite, granodiorites, and syenite. As no fragments of these are found in the Gympie and as that formation is metamorphosed, the granitic rocks are believed to be later than the Gympie. The gold deposits are older than the Desert sandstone, for the lower beds of that sandstone contain detrital gold derived from the Mount Morgan lode. Wilson regards the granitic intrusions as agents of fracturing and mineralization.

The ore deposits are in quartzites and graywackes of the Gympie, not far from the contact with granitic rocks. Four large dikes and many smaller ones cut the ore. As a whole the principal deposit may be considered a wide fractured zone. The outcrop of the deposit that formed the summit of the hill consisted of limonite, kaolin, manganese oxide, and cellular silica, and carried considerable gold. The depth of the oxidized zone is 180 to 300 feet. It yielded 1 to 5 ounces to the ton, and in places was exceedingly rich. The gold was 0.998 fine. Locally silver was concentrated in kaolinic ore. Farther down there was an ore of pyrite and chalcopyrite containing 2.5 to 3.5 per cent of copper and $1 to $8 gold. The change from oxidized to unoxidized ore is abrupt and in places the transition zone is not over 10 feet wide.[1]

A set of specimens of ore from this mine was recently supplied to me through the courtesy of Mr. H. Eidemiller. The unaltered ore, which is doubtless primary, consists of pyrite with a little chalcopyrite intergrown with quartz. Some of the quartz is white and some is brownish, its color being due to manganese. Probably the source of the manganese, which appears to be abundant in the upper part of the deposit, is the manganiferous quartz. A little chloritic material is intergrown with the pyrite. This ore exhibits a rude banding. A magnet passed over the crushed unaltered material does not reveal either magnetite or pyrrhotite. Wilson[2] states that the ore includes a little sphalerite.

Another specimen from the district is partly oxidized. It is covered with limonite, through which small particles of gold are scattered and crystals of malachite and azurite are conspicuously developed. The specimen, when broken, was seen to be a mass of chalcocite surrounded by limonite. The chalcocite contains numerous small particles of pyrite, which doubtless have altered to supply iron for the limonite that surrounds the chalcocite. A little manganese dioxide is mixed with the limonite and gold. Considerable calcite, in a finely divided state, is found in both chalcocite and limonite ore. Particles of gold are numerous in the sponge of limonite that surrounds the chalcocite, and at one place a thin plate of rich yellow gold covers the chalcocite. It is said that this ore is so rich that it is

[1] Wilson, J. B., op. cit., p. 98. [2] Idem, p. 97.

used directly in copper converters without preliminary smelting. (See fig. 22.)

This region is near the sea and the waters doubtless carry chlorides. Some manganese is present, and the conditions are therefore favorable for the solution of gold. Undoubtedly gold has been dissolved, for it coats secondary minerals, but its solution has not quite kept pace with erosion, for some gold is found in Cretaceous beds near by, and the outcrops of the deposit are rich. There is much evidence, however, that the bonanza surface ore is due to solution and reprecipitation.

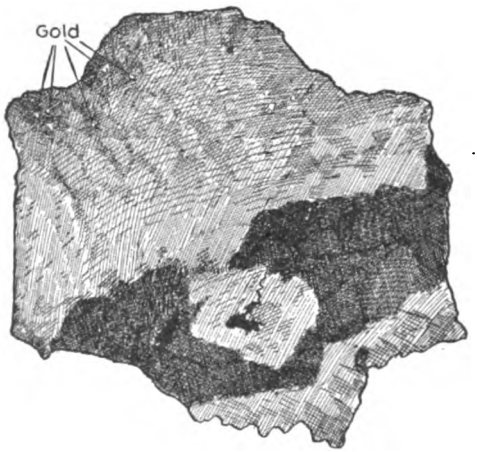

FIGURE 22.—Ore from Mount Morgan mine, Queensland. The dark band is chalcocite and calcite, the light is limonite and white spots are gold.

The descriptions indicate that the rich oxidized gold ore in the upper part of the mine may be in part the remnant of an oxidized chalcocite ore, rich in gold, and that the solutions have brought about a segregation of gold and chalcocite in the deposit by the same processes that have segregated the gold and copper in the specimen here described. A noteworthy feature of this ore is the association of chalcocite and calcite, which are contemporaneous. They are doubtless secondary, for chalcocite in this deposit is not found in depth.

CRIPPLE CREEK, COLORADO.

The gold deposits of Cripple Creek, Colo., are fissure veins and replacement deposits in volcanic breccia, in alkali-rich and other Tertiary intrusive rocks, and in granite. The fissures, according to Lindgren and Ransome,[1] were formed at about the time of the intrusion of the associated basic dikes and represent a late phase of volcanic activity. The deposits are probably of middle or late Tertiary age and were formed relatively near the surface by hot ascending waters. Calaverite is the chief primary constituent; native gold is rarely present in the unoxidized ores. Pyrite is widely

[1] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 167–168, 1906. Cross, Whitman, and Penrose, R. A. F., jr., Geology and mining industries of the Cripple Creek district, Colorado: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, pp. 1–209, 1895. Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, pp. 193–252, 1904. Rickard, T. A., The Cripple Creek volcano: Am. Inst. Min. Eng. Trans., vol. 20, pp. 462–545, 1891.

distributed; tetrahedrite, stibnite, sphalerite, and molybdenite are sparingly present. The gangue is quartz, fluorite, adularia, carbonates (including rhodochrosite), some sulphates, and other minerals. Some of the deposits were workable at the surface, but the placers formed are relatively unimportant. Although rhodochrosite is subordinate in amount, the highly fractured country rock contains appreciable manganese (0.2± per cent). According to Lindgren and Ransome, the processes of oxidation were attended by the formation of kaolin, hydrous silica, and oxides of iron and manganese. Manganese oxides are commonly present in the oxidized zone[1] and, according to Penrose, form nodules in the Pharmacist and Summit mines. They result from the alteration of rhodochrosite, manganiferous calcite, or other minerals and are generally distributed in the oxidized zone as stains in cracks and fissures.[2] During oxidation manganese is greatly concentrated in the seams of the rock. In general, the lower part of the zone of oxidation is above water level and is usually less than 200 feet below the surface. In some places silver has been completely leached from the oxidized ores. Horn silver has not been noted.

Whether a slight enrichment of gold has taken place in the oxidized zone is not easy to demonstrate. Lindgren and Ransome are inclined to the belief that the oxidized zone as a whole is somewhat richer than the corresponding telluride zone.[3] The trivial enrichment in this zone may have resulted from the removal of some constituents of the primary ore.

If gold was dissolved in the Cripple Creek deposits, it was precipitated again at practically the same horizon, for in these deposits the zone in which solution takes place is rich. The ground is open, providing paths for downward-circulating waters, but although the ore-bearing complex is very pervious to water it is surrounded by impervious rocks. After the volcanic rocks had been drained in mining the flow of water was comparatively small. Lindgren and Ransome have compared the volcanic complex to a "sponge in a cup." As shown by them, the conditions were unfavorable for the circulation of atmospheric water, a fact which had an important bearing on their conclusion that the ores had been formed by magmatic waters. In the absence of a circulation the gold could not be transported. A check to this reasoning with respect to a downward circulation is the fact that in the porous, brecciated mass, filled with stagnant water, the oxidation extended downward to a depth generally less than 200 feet, and even in this zone residual sulphides are present. If the solutions did not carry oxygen downward it would be supposed

[1] Penrose, R. A. F., Mining geology of the Cripple Creek district, Colorado: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 123, 1895.

[2] Lindgren, Waldemar, and Ransome, F. L., op. cit., p. 123.

[3] Idem, p. 203.

that they could not carry gold, and even if the gold had been dissolved at the higher levels, in the absence of a circulation it could not descend. Some of the deposits are in rocks containing nepheline and other alkali-rich minerals. Such minerals, as shown by Nishihara (p. 121), neutralize acid very readily and any solution carrying gold would precipitate it as soon as acidity is reduced. There is some evidence which may be interpreted as an indication that the gold migrated laterally, or possibly that it was precipitated essentially in place from cold solutions. Richard Pearce[1] has recorded analyses of oxidized and unoxidized ore. The material for the analyses was taken from a section drawn clear across the two different portions of the specimen. The analyses show that the oxidized ore carries 14.58 ounces of gold per ton, or 2.34 ounces more gold than the unoxidized ore, and that all the silver has been leached out. In ore so rich such a concentration may result merely from leaching out of the substances other than gold; but, on the other hand, the analyses of the altered rock indicate that little leaching of the silicate minerals has taken place and that the oxidized portion was originally richer than the unoxidized, or else that some gold had been added. Since 0.27 per cent of manganese dioxide is present in the oxidized ore, whereas none is reported in the unoxidized ore, it appears that manganese dioxide was added in the process of secondary alteration, and it is possible that the same solutions added gold and iron. J. W. Finch[2] regards some of the gold as secondary.

If the gold was dissolved in the Cripple Creek "sponge," it may have been precipitated in the nearly stagnant solutions where they were in contact with pyrite or other minerals. In the absence of a downward circulation of water such lateral migration would be possible.

The results of oxidation processes are described by Lindgren and Ransome[3] as follows:

> Thorough oxidizing decomposition will destroy the original structure of this vein. In sheeted lodes with many small parallel fissures and joints the latter may become effaced and the lode appears as a homogeneous brown soft mass. In other cases a central seam may be retained and usually appears as a streak of soft, more or less impure kaolin; in other cases it may be filled by white compact alunite, more rarely by jasperoid or opaline silica. Crusts of comb quartz, if originally present, lie included in the clayey seams, but neither the original fluorite nor the carbonates are ordinarily preserved. Very rich oxidized ore sometimes fills the central cavities of the lode like a thick, brown mud of limonite, kaolin, and quartz sand and easily flows out when the vein is opened.

[1] Pearce, Richard, Further notes on Cripple Creek district: Colorado Sci. Soc. Proc., vol. 4, pp. 11–16, 1896.

[2] Finch, J. W., The circulation of underground aqueous solutions and the deposition of lode ores: Colorado Sci. Soc. Proc., vol. 7, pp. 193–252, 1904.

[3] Lindgren, Waldemar, and Ransome, F. L., op. cit., p. 199.

It should not be inferred, however, that where channels are large and open the rich, gold-bearing brown mud is necessarily a deposit from solution. It may have been carried down in suspension; for similar rich mud, with 2 ounces of gold per ton, was found on the floor of the twelfth level of the Gold Coin mine after it had been filled with water and allowed to stand.

It thus appears that the conditions at Cripple Creek, which are somewhat puzzling, may be rationally explained if it is noted that the downward migration of gold requires not only solution and precipitation but also circulation, and that the conditions for circulation here were peculiarly unfavorable. The facts show also that a relatively rapid circulation is required to carry dissolved gold far below the zone of mixed oxides and sulphides, particularly in rocks containing feldspathoids, which, as shown by Nishihara, reduce acidity of solutions with great rapidity.

GOLDFIELD, NEVADA.

The ledges of Goldfield are in middle or late Tertiary rocks and, according to Ransome,[1] were probably deposited within 1,000 feet of the Tertiary surface. Ransome states convincingly the hypothesis that these deposits were formed by hot ascending solutions which mingled with descending sulphate water that contained oxygen derived from the air. Although the deposits are probably the most remarkable bonanzas of native gold ores carrying little silver which have yet been discovered, it does not appear that they have been very greatly enriched since they were deposited, for, as remarked by Ransome, it is difficult to harmonize the extent and intensity of alunitization in the gold ores with the hypothesis that the ores were formed by the oxidation and enrichment of lean deposits during erosion. The mine waters are rich in sulphates and, judging from the geographic position of the deposits, probably carry chlorides. Manganese dioxide is practically unknown in these ores, which in this respect differ from the ores at Tonopah and from a great many other Tertiary deposits of the Great Basin province. No workable placer deposits have been discovered; yet, notwithstanding the fact that several hundred feet of vein matter may have been removed from these deposits since they were formed, there is little reason to suppose that much gold has migrated into the existing bonanzas from above. The gold is very finely divided and could have been scattered if it had been eroded with the ledges. Analyses of deposits elsewhere that were formed close to the surface by ascending hot waters show that few of them carry much gold. The zone of maximum deposition is lower down, for as soon as the ascending

[1] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 174, 1909.

hot waters are contaminated by ferrous sulphate from the surface waters the gold they contain must be precipitated.

The evidence offered at Goldfield is not out of harmony with the conclusion that in the absence of manganese gold is not readily transported in mine waters.

SUMMARY REVIEW OF SEVERAL CLASSES OF COPPER, GOLD, AND SILVER DEPOSITS.

A number of the principal sulphide deposits of copper, gold, and silver have now been briefly described, in order that the several districts may be compared to ascertain the extent, character, and distribution of the secondary ores in them. As already stated, many of the problems arising in this connection are now only in process of solution, yet by grouping these deposits in several ways, certain facts are clearly indicated. The conclusions stated below appear to be warranted by the data here presented.

COPPER DEPOSITS IN GENERAL.

The deposits of many copper districts do not show appreciable chalcocite enrichment. Examples are Kasaan Peninsula, Alaska; Prince William Sound, Alaska; Sudbury, Ontario; Boundary district, British Columbia; Copperopolis, Cal.; Frisco, Utah (Cactus mine); La Reforma mine, Mexico; probably San Jose, Velardeña, and Nacozari, Mexico. The mines of the Braden Copper Co., operating in Chile, may be added to this list. Deposits showing no chalcocite enrichment, in countries that have recently been glaciated, include those of Kasaan Peninsula and Prince William Sound, Alaska; Sudbury, Ontario; Boundary district, British Columbia. Some deposits that show very little chalcocite enrichment are found in countries that, so far as I can discover, have not recently been glaciated, as at La Reforma, Copperopolis, Nacozari, Ajo, and San Jose. Deposits that contain no appreciable chalcocite zones are found in countries in widely different latitudes—Alaska, British Columbia, Ontario, California, Utah, Arizona, Mexico, and Chile. Deposits that contain no appreciable chalcocite zone exhibit primary ores containing pyrrhotite, such as those of Kasaan Peninsula and Prince William Sound, Alaska; Sudbury, Ontario; and the Boundary district, British Columbia. They also exhibit primary ores, in the available descriptions of which pyrrhotite is not reported, as the La Reforma; Copperopolis; Cactus mine, Utah; Nacozari (some bornite enrichment); San Jose; Velardeña, Mexico; Braden, Chile.

All the pyrrhotitic deposits which do not exhibit secondary chalcocite zones are in recently glaciated areas. Some of these deposits carry sphalerite. All the deposits described that are in lower lati-

tudes and that show no appreciable chalcocite enrichment have primary ores of pyrite and chalcopyrite. Zinc blende is absent or not abundant in most of these deposits, but Velardeña (Copper Queen mine) and Frisco (Cactus mine) are exceptions. Possibly there are some others. In none of these deposits is pyrrhotite reported. In glaciated areas oxidized ores for this group are subordinate or lacking. In areas not glaciated a few of the deposits exhibit oxidized ores of commercial value. In all or nearly all the deposits in low latitudes that show no appreciable chalcocite enrichment complete oxidation has proceeded to comparatively shallow depths. The lodes in general are said to be relatively impervious. The copper sulphate solutions probably move laterally and issue at the surface before they encounter reducing conditions, or they escape into the wall rock and their copper content is scattered. La Reforma is a good example. At Ajo, Ariz., oxidation is extensive, but the secondary chalcocite zone is relatively insignificant, perhaps because the primary copper ores carry little pyrite or other iron sulphides.

I know of no pyrrhotitic copper deposit in a low latitude or in a country not glaciated that shows no chalcocitization. Pyrrhotite reacts so readily with acid to give hydrogen sulphide that acid solutions may be reduced and copper sulphide may be precipitated even with access of some air. Copper sulphide is now being precipitated on ore surfaces in mines of Ducktown, Tenn., above the present water level. Such precipitation probably does not take place at the higher levels on pyrite and chalcopyrite.

The copper content of some of the pyrrhotitic deposits in glaciated areas decreases with increase of depth. Possibly a former chalcocite zone was planed off by the ice and a secondary chalcopyrite zone was not completely removed, as is strongly suggested by relations in the Boundary district, British Columbia.

COPPER DEPOSITS WITH SHALLOW CHALCOCITE ZONES.

Many copper deposits exhibit shallow chalcocite zones. These include Ducktown, Tenn.; Stone Hill, Ala.; Gossan lead, Virginia; Queen of Bronze mine, Oregon; Santiago, Cuba; Pinar del Rio, Cuba; La Dicha, Mexico; and possibly Encampment, Wyo.; and the Highland Boy mine of Bingham, Utah. All of these are outside of the limits of the continental ice sheets. A deposit on Prince William Sound, Alaska, however, shows a few inches of secondary sulphide ore. The ores of all these deposits carry pyrrhotite. In most of them it is abundant.

The chalcocite zones of most of the deposits of this group are thin, ranging in vertical dimensions from 1 foot to 10 feet. In some of the deposits, however, their vertical extent is 100 feet or possibly more.

As a rule the secondary chalcocite ores of these deposits are rich. Some of them carry over 20 per cent copper. Gold or gold and silver are very commonly concentrated in the secondary copper ores.

A zone of chalcopyrite enrichment may exist below the chalcocite zone, and it may be of considerably greater vertical extent than the secondary chalcocite zone, as in the deposits at Ducktown, Tenn.; Rio Tinto, Spain; and possibly others. Pay ores are commonly found below the zone of probable chalcopyrite enrichment, and some of them are of moderately high grade. Few, if any, however, could be classed as bonanza.

COPPER DEPOSITS WITH MODERATELY DEEP CHALCOCITE ZONES.

In many deposits of copper sulphide ores secondary chalcocite extends to moderately great depths. Examples are Morenci, Globe, Miami, Ray, and Jerome, Ariz.; Santa Rita (Chino), N. Mex.; Ely, Nev.; Bingham, Utah (in part); Cananea, Sonora (in part); Butte, Mont. In many of these deposits the vertical extent of the chalcocite zone is from 200 to 1,000 feet or more. These deposits are outside of the margins of the continental ice sheets, and many of them are in countries now arid. No pyrrhotite is found in the ores of these deposits.

The primary ores of several of these districts carry appreciable sphalerite. Examples are Morenci, Metcalf, Jerome?, Cananea (West Cobre Grande and Kirk). At Morenci and Metcalf the bulk of the chalcocite is within 400 feet of the surface. In the West Cobre Grande chalcocite passes into low-grade zincky ores about 200 feet below the surface. Exact data are not available for Jerome and for certain Bingham mines.

The deepest secondary chalcocite zones are in ore bodies that contain little or no pyrrhotite or sphalerite. Examples are Globe and Miami, Ariz.; Bingham laccolith, Utah; Butte, Mont. (in part). A few deposits of this character have chalcocite zones that probably are not of much greater vertical extent than chalcocite zones in some sphalerite deposits. Examples are Ray, Ariz., and possibly Santa Rita (Chino), N. Mex. Zones of chalcopyrite enrichment below the zones of chalcocite have not been clearly differentiated in any of these deposits.

COPPER DEPOSITS WITH DEEPLY OXIDIZED ZONES.

Copper deposits that contain deeply oxidized zones include many of those of Tintic, Utah, and Bisbee, Ariz.; some of Bingham, Utah; and the Snowstorm mine of the Coeur d'Alene district, Idaho. None of these deposits are known to carry pyrrhotite. The data here presented indicate that in general oxidized zones above ores containing

abundant pyrrhotite are more thoroughly oxidized than those above ores containing pyrite and chalcopyrite without pyrrhotite, but such oxidation is not likely to extend to depths so great in pyrrhotite ores. The pyrite ores of Rio Tinto, Spain, those of La Reforma mine, Mexico, and some of the deposits at Butte, Mont., are capped by thoroughly oxidized material; possibly there are others.

The deepest zones of oxidized copper ores are in deposits in limestone. Examples are at Tintic, Utah. Not all the deeply oxidized zones of copper ores are in arid countries (Snowstorm mine, for example).

The vertical extent of chalcocite enrichment and the depth of oxidation depend upon the permeability of the deposits, the chemical and mineral composition of the ores and wall rock (p. 172), the present and the past climatic environment, and the geologic history. At Bisbee, Ariz., an ancient oxidized zone has been tilted since the ores were altered.

GOLD DEPOSITS EXHIBITING SECONDARY CONCENTRATION.

Many auriferous deposits in the surficial zone appear not to have been enriched by secondary agencies. The distribution of valuable deposits in the lodes of Berners Bay and Douglas Island, Alaska, shows no relation to the present surface. In this glaciated region there has been little or no concentration of gold at the surface by the removal of valueless material from the outcrops.

There is no evidence of solution and reprecipitation of gold in some other auriferous deposits in lower latitudes, although there may be an increase of values at the outcrop through oxidation that is attended by the removal of the material with which the gold is associated. Examples are Mother Lode, Nevada City, Grass Valley, Ophir, and similar deposits of California; Homestake deposits of the Black Hills; Cable mine, between Philipsburg and Anaconda, Mont.; and several deposits in the Appalachians. Practically all the important deposits in these regions have supplied placer gold. There are still other deposits whose relations do not indicate a migration of gold and from which no placers have been exploited. Examples are Edgemont, Nev.; Goldfield, Nev.; Silver Peak, Nev.; Cripple Creek, Colo. (subordinate placers). Not all of these are in arid regions, Edgemont and Cripple Creek being moderately well watered.

Solution, migration, and reprecipitation are clearly indicated in a number of auriferous deposits. In some of them this is inferred from paragenetic evidence, in others from the great richness of the bonanzas compared with the unaltered ore together with the relations of the bonanzas to the present surface. Examples are found at Creede,

Colo. (Amethyst vein); Ouray, Colo. (Camp Bird vein); Telluride, Colo. (Tomboy vein); some veins in quartzite near Leadville, Colo.; Little Burro Mountains, N. Mex. (Wyman vein); Bodie, Cal.; Bullfrog, Nev.; Manhattan, Nev.; Gold Circle, Nev.; Mohave, Cal. (Exposed Treasure vein); Georgetown, Colo. (auriferous lodes?); Marysville, Mont. (Drumlummon veins). All the deposits named above carry manganese.

Four districts are described herein in which gold has migrated in solution in ores that are not stated to carry manganese. Two of these (Haile mine, South Carolina, and Hedley district, British Columbia) are in regions of basic rocks, which possibly supply manganese to the solutions. Two others (Bohemia district, Oregon, and Summit district, Colorado) are in acidic and intermediate rocks. Manganese is not mentioned as a vein constituent in the descriptions that are available to me.

The outcrops of manganiferous gold ores are commonly leached, and placer deposits are not so frequently developed from them as from nonmanganiferous lodes. This is apparent from the inspection of the lists above. Two examples are conspicuous exceptions—Marysville, Mont., and Mount Morgan, West Australia. Both have enormously rich deposits, practically at the surface; both have supplied placer gold. The unaltered ores of Marysville carry calcite, which reduces auriferous solutions very rapidly. Some calcite is present also in copper sulphide ore at Mount Morgan. Some rich manganiferous gold ores are found very near the surface at Bullfrog and Manhattan, Nev. At both places the gangue is calcite.

It is concluded that the solution of gold depends in the main on the presence, simultaneously, of manganese and chlorides. Its migration depends on the permeability of the lodes and the material of the primary ores. Of the common minerals, calcite and pyrrhotite will reduce auriferous solutions most rapidly. All carbonates and feldspathoids are effective. The action with pyrite and chalcopyrite is less efficient. (See p. 314.)

SILVER AND SILVER-GOLD DEPOSITS.

Enrichment is clearly indicated in a number of silver and silver-gold deposits. Examples may be found at Georgetown, Breckenridge, Leadville, Aspen, Silverton, Creede, and Lake City, Colo.; at Philipsburg, Butte, and Neihart, Mont.; on the Comstock lode, at Tonopah, and at Pioche, Nev.; at Mohave, Cal.; and in the St. Eugene mine at Moyie Lake, British Columbia. In several of these districts, but not in all, a migration of gold also is clearly indicated. All the districts of silver-gold deposits in which gold is assumed to have migrated have manganiferous ores.

In deposits carrying both metals, especially where chlorides form, secondary silver minerals are likely to be precipitated as bonanzas near the surface, while gold may be carried to greater depths. Examples are deposits of Mohave, Cal. (Exposed Treasure mine), Creede, Colo. (Amethyst lode), and probably the Comstock lode, Nevada, although in the Comstock district and at Creede silver chloride is not abundant.

In manganiferous deposits of gold and silver, where chlorides do not form extensively, silver is carried downward to greater depths than gold, especially where the ores carry carbonates. These precipitate gold instantly and completely, but the carbonates do not precipitate silver from sulphate solutions unless the solutions are concentrated. Then some, but not all, of the silver is precipitated.

Abundant pyrrhotite in the primary ore quickly halts the downward migration of both silver and gold. Some of the secondary ore of the "black copper floors" of Ducktown, Tenn., carried considerable silver. A sample assay by Genth showed over 1 per cent. Not many examples are available, probably because the pyrrhotitic ores carry copper and the rich superficial concentrations were worked out before the days of electrolytic refining. Since acid waters generate hydrogen sulphide on pyrrhotite almost immediately, and since hydrogen sulphide precipitates gold and silver perhaps completely, the gold and silver could not descend to any considerable depth in pyrrhotitic ores. Although the principal ore deposits of Rio Tinto, Spain, carry little or no pyrrhotite, and although zinc blende is not abundant in most of them, they should be mentioned here. Above one of the principal deposits there is a "floor" of rich silver and gold ore at or just above the top of the chalcocite zone.[1] Moreover, chalcocite itself will quickly and completely precipitate both gold and silver. In copper deposits where silver and gold migrate downward the precious metals are precipitated in the upper part of the zone of secondary copper sulphides rather than in the lower part.

Many deposits of rich silver ore and some deposits of rich silver-gold ore terminate downward in low-grade sphalerite ores. Abundant examples are to be found in the regions of Georgetown, Breckenridge, Creede, and Lake City, Colo.; Pioche, Nev.; and Lake Moyie, British Columbia. In most of these districts the bonanzas of silver ores are comparatively near the surface. In the Comstock lode and at Tonopah, Nev., and in the Granite-Bimetallic vein at Philipsburg, Mont., a little zinc is present, but not much. In these the richer ores are found at greater depths. At Creede, Colo., in the Amethyst vein, secondary silver ore has been formed at greater depths than is usual in the region of Georgetown and Breckenridge,

[1] Vogt, J. H. L., Das Huelva-Kiesfeld: Zeitschr. prakt. Geologie, p. 250, 1899. Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, p. 410, 1910.

notwithstanding the fairly abundant zinc sulphide in the primary ore at Creede. This, I believe, is to be explained by excessive fracturing of the Amethyst vein, which at some places is little more than an ore breccia.

A conspicuous example outside of America of a deposit of rich silver-lead ore passing into low-grade sphalerite ore in depth is the great Broken Hill lode of New South Wales. This deposit is in schists and in general conforms to the schistosity. Judging from the drawings of Capt. Warren,[1] it resembles in certain structural features the broken folds of some of the deposits of Ducktown, Tenn. Though classed as a saddle reef by J. B. Jaquet[2] on account of its bifurcating structure, it may be considered, for the purpose of this discussion, a tabular mass, since the bifurcation of the lode is shown between the 415 and 515 foot levels, from which point it extends to the surface as a tabular body. Without much doubt a considerable amount of the lode has been eroded, and the valuable metals appear to have concentrated in the remaining portion relatively near the surface. Siliceous limonitic manganitic ore is said to have extended from the surface to about 300 feet below. This ore was 20 to 100 feet wide and, according to Phillips and Louis,[3] carried 7 to 45 ounces silver and 18 per cent lead. At the bottom of this siliceous ore was a narrow zone of kaolinic ore, portions of which carried great bonanzas of silver, largely in the form of chloride. Below this level, on block 10, at a depth between 400 and 500 feet below the surface, were rich friable sulphides with galena and zinc blende. Below the rich friable sulphides values decreased greatly, the ore being composed of "compact sulphides, or an intimately mixed mass of galena and blende, with a gangue of quartz, rhodonite, and garnet." I have no record that pyrrhotite is present in these ores, though it is mentioned as abundant in the Pinnacles mine, 9 miles southwest of Broken Hill.

Calcite, as stated above, will precipitate gold at once from gold-bearing chloride solutions. Consequently deposits of gold with calcite gangue are not likely to be enriched to great depths, at least not until most of the calcite is dissolved and removed along the passages through which the gold-bearing solutions descend. In general, calcitic gold deposits are not enriched to great depths. But the carbonates do not precipitate silver from dilute sulphate solutions and not completely from moderately concentrated sulphate solutions. Silver can be transferred to the deeper parts of deposits that have carbonate gangue unless the gangue contains the very active sul-

[1] Reminiscence of Broken Hill, quoted by Clark, Donald, Australian mining and metallurgy, Melbourne, 1904. The original is not accessible to me.

[2] Jaquet, J. B., Geology of the Broken Hill lode and Barrier Ranges mineral field, New South Wales: Geol. Survey New South Wales Mem., Geology No. 5, 1894.

[3] Phillips, J. A., A treatise on ore deposits, 2d ed., by Henry Louis, p. 655, 1896.

phides, such as pyrrhotite, alabandite, and niccolite. Indeed, the gangue of nearly all deeply enriched silver deposits, including most of the largest silver deposits of the world, contains carbonates (p. 257).

Although the chemical and mineral environment at depth has been emphasized in the foregoing discussion, the permeability of the primary ores is also an important factor in determining the depths to which the metals may descend, whatever the character of the primary sulphides.

LEAD.

PRINCIPAL LEAD MINERALS.

The chemical composition of the principal lead minerals is given below:

Lead.....Pb.
Minium..... $2PbO.PbO_2$.
Massicot.....PbO.
Plattnerite.....PbO_2.
Pyromorphite...$Pb_5P_3O_{12}Cl$.
Cotunnite.....$PbCl_2$.
Phosgenite.....$PbCO_3PbCl_2$.
Beaverite.....$CuO.PbO.Fe_2O_3.2SO_3.4H_2O$.
Corkite.....A hydrous phosphate and sulphate of lead and iron.
Linarite..... $(PbCu)SO_4.(PbCu)(OH)_2$.
Plumbojarosite..$Pb[Fe(OH)_2]_6[SO_4]_4$.
Leadhillite.....$4PbO.SO_3.2CO_2.H_2O$.
Bindheimite.....$Pb_3Sb_2O_8.+aq$.
Anglesite..... $PbSO_4$.
Cerusite..... $PbCO_3$.
Hinsdaleite.....$2PbO.3Al_2O_3.2SO_3.P_2O_5.6H_2O$.
Bournonite.....$PbCuSbS_3$.
Jamesonite.....$Pb_2Sb_2S_5$.
Galena.....PbS.

SOLUBILITIES OF LEAD COMPOUNDS.

The solubilities of several lead compounds, as determined by Kohlrausch, are as follows:

$PbSO_4$.	$PbCl_2$.	$PbCO_3$.	$Pb(NO_3)_2$.
0.041	14.9	0.001	516.6
.00013	.05	.00003	1.4

The upper number in each column shows the number of grams of the anhydrous salt held in solution in a liter of water at 18° C.; the lower number shows the molar solubility or the number of mols contained in a liter of the saturated solution.[1]

[1] Smith, Alexander, Introduction to inorganic chemistry, rev. ed., p. 544, 1910.

The common salts of lead are bivalent; the rarer ones are quadrivalent. As shown by the table above, all the common salts have low solubilities except the nitrates, which are not important in processes of sulphide enrichment. Freshly precipitated lead sulphide is dissolved sparingly in cold water, its solubility being 0.0000036 mol in a liter. (See p. 117.)

NATURE AND RELATIONS OF LEAD MINERALS.

The native metal and the oxides of lead (minium, plattnerite, and massicot) are of rare occurrence.

Lead chloride is moderately soluble, so cotunnite, $PbCl_2$, does not accumulate in the oxidized zones of lead deposits. Lead chlorophosphate, pyromorphite, is much more common. Perhaps a dozen other minerals of lead and chlorine are formed in oxidized zones, but all are rare. Lead carbonate is very sparingly soluble, so cerusite, $PbCO_3$, is a comparatively stable mineral, as is the sulphate, anglesite, $PbSO_4$. Although the solubility of the sulphate is low, it is nevertheless appreciable, as is indicated in quantitative analysis, for in order to prevent loss a precipitate of lead sulphate formed in sulphuric acid is washed with alcohol rather than with water. The transfer of lead as sulphate in small yet appreciable quantities was shown also in the experiments of Buehler and Gottschalk (p. 109). H. C. Cooke[1] found that a gram of galena in contact with sulphuric acid and ferric sulphate gained (by oxidation) 0.17 gram in 81 days; in acid alone it gained only 0.0714. Some specimens of galena react readily with dilute sulphuric acid and yield hydrogen sulphide, but the reaction is not sustained. It is due to minute quantities of included manganese sulphide, probably alabandite.[2]

As would be supposed from consideration of the relatively low solubility of its sulphate, lead is not extensively transferred in cold sulphuric acid waters. Whether oxygen is necessary for the solution of lead sulphide, as it is for the solution of copper sulphide, I am unable to state. The salts that form under natural conditions have low solubilities and coat the sulphides, inhibiting or at least retarding further action. Consequently lead sulphide dissolves slowly. It is dissolved in acid to only a slight extent and, like copper sulphide, could be deposited in an acid environment. Although several primary minerals contain lead, galena is the only one of these that is at all common. Bournonite and jamesonite are both primary. Possibly hinsdaleite also is a primary mineral formed near the surface.

All the other minerals listed above—the chlorides, oxides, sulphates, and carbonates—are probably formed as secondary minerals

[1] Cooke, H. C., Secondary enrichment of silver ores: Jour. Geology, vol. 21, p. 11, 1913.

[2] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 747, 1914.

only. The sulphate anglesite forms by oxidation of galena, as shown in figure 23. The process begins along cracks, from which it gradually extends outward. The carbonate at many places is formed from anglesite, and ordinarily galena is surrounded by a shell of anglesite, which is coated with carbonate. Figure 24 is a drawing of such an ore. Many other examples are mentioned on page 362.

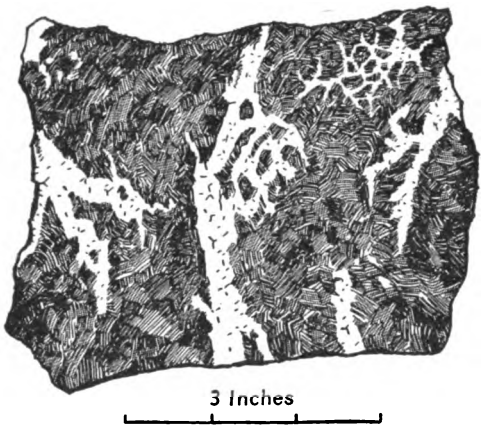

FIGURE 23.—Galena (dark) altering to anglesite (light) along cracks. Ore from 1,000-foot level in Park Regent mine, Amethyst vein, Creede, Colo. After W. H. Emmons and E. S. Larsen.

As shown by Wells,[1] the carbonate of lead is one of the most stable carbonates of the common metals. Mercury only is precipitated more readily by soluble carbonates. It could readily replace all the other common carbonates if the insolubility of its salts did not prevent its extensive solution and transportation.

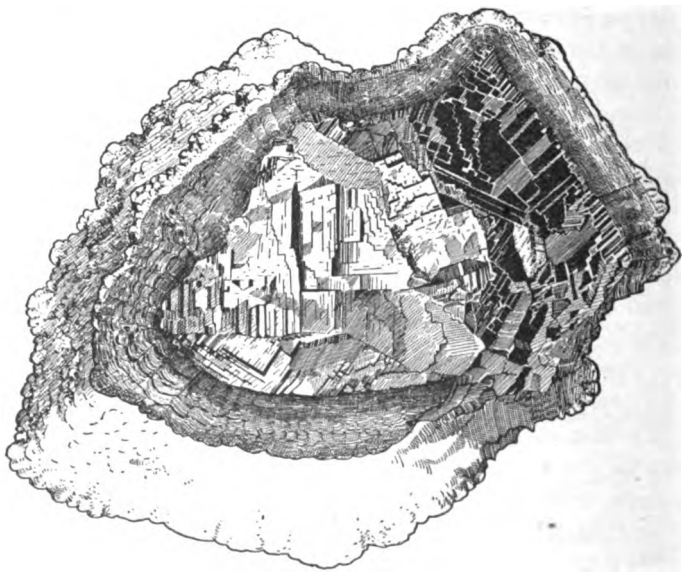

FIGURE 24.—Nodule of galena altering to anglesite. A little cerusite is present in the outer shell. Last Chance mine, Amethyst lode, Creede, Colo. After W. H. Emmons and E. S. Larsen.

A study of the paragenesis of galena and associated minerals affords scant evidence that it is commonly precipitated below the

[1] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

water level in lode ores, but it is regarded as primary in the greater number of its deposits. According to Butler it replaces sphalerite at the Horn Silver mine, Utah,[1] and a few other examples of its secondary deposition are known (p. 140). Lead, like gold, migrates very slowly in cold solutions. The oxidation of sulphides of lead, zinc, and iron is discussed on page 374.

OCCURRENCE OF LEAD MINERALS.

Native lead.—Although native lead is found in a number of lead deposits,[2] it is in very few so abundant as to become an important ore mineral. It is probably formed by reduction of oxygen salts of lead.

Minium, Pb_3O_4, red lead, is a comparatively rare oxidation product of lead ores. It has been found in Lemhi County, Idaho,[3] as red powder filling little cavities near the surface. A little is found, also, at Tintic, Utah,[4] and at Telluride, Colo.[5] At many lead mines it has not been noted.

Massicot, PbO, a yellow lead oxide, though more abundant than native lead, is a comparatively rare mineral. It is an oxidation product of galena and other lead compounds. In the Coeur d'Alene district, Idaho, it occurs as a yellow powder in some oxidized lead ores associated with cerusite.[6] It is found in considerable abundance near the top of ore shoots in the Caledonia mine.[7] In Mexico, between Monterey and Ceralvo,[8] it has collected in considerable quantity in gravels along the streams.

In the Park City district, Utah, according to Boutwell,[9] massicot is associated with altered lead ore in patches on altered galena and in some places along fractures penetrates the mass itself. This oxidation was found in all stages in the Silver King mine on the 1,200-foot level. In places the ore, which has been very completely oxidized, appeared to lie along bedding planes. Massicot is associated also with the carbonates of lead and copper, the sulphate of lead, and the primary minerals galena and tetrahedrite. It is spar-

[1] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[2] Hintze, Carl, Handbuch der Mineralogie, Band 1, pp. 333–334, 1904.

[3] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 78, 1913.

[4] Tower, G. W., and Smith, G. O., Geology and mining industry of Tintic, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 696, 1898.

[5] Purington, C. W., Preliminary report on the mining industries of the Telluride quadrangle, Colorado: U. S. Geol. Survey Eighteenth Ann. Rept., pt. 3, p. 794, 1897.

[6] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 94, 1908.

[7] Shannon, E. V., Secondary enrichment in the Caledonia mine, Coeur d'Alene, Idaho: Econ. Geology, vol. 8, p. 569, 1913.

[8] Dana, J. D., System of mineralogy, 6th ed., p. 209, 1892.

[9] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 110, 1913.

ingly developed in the Texas district, Idaho.[1] Some probably occurs in oxidized ore at Goldfield, Nev.[2]

Plattnerite, PbO_2, like minium, is a rare mineral formed in oxidized zones of some lead deposits. It occurs in the You Like mine, Coeur d'Alene district, with pyromorphite and limonite. There are perhaps only two or three reported occurrences of this mineral.[3]

Pyromorphite, $Pb_5P_3O_{12}Cl$, is the principal metallic phosphate, and is the only common lead mineral that contains chlorine. It is an alteration product of lead ores that are exposed to waters carrying chlorine and phosphoric acid, and is frequently developed in outcrops of lead deposits. At Philipsburg, Mont.,[4] at Creede, Colo., and in the Coeur d'Alene district, Idaho,[5] it is characteristic of the upper parts of the zones of oxidation. In these deposits it is associated with limonite and commonly carries silver, possibly as finely divided cerargyrite. According to Rogers,[6] a specimen of galena ore from Granby, Mo., is altered to cerusite, which is bordered by pyromorphite. A little pyromorphite is found in the ores of the Texas district, Lemhi County, Idaho.[7] At Yellow Pine, Nev.,[8] pyromorphite is found in the croppings of the lead-zinc ores, mixed with cerusite, hydrozincite, and smithsonite.

Crystals of pyromorphite, yellow and green, are found in the Society Girl mine, British Columbia, southeast of the St. Eugene mine, Moyie Lake. (See p. 291.) The pyromorphite is associated with galena and cerusite. Bowles[9] thinks the green color is due probably to arsenic,[10] which is present in small quantities.

Cotunnite, $PbCl_2$, as already stated, is a comparatively rare mineral. It has been identified at a few places, one of them in the crater of Vesuvius. A lead chloride, probably cotunnite, occurs at Grand Gulch, Ariz., as a replacement of chalcocite in a specimen collected by Hill.[11] Its minute branching veinlets cut the chalcocite. Lead

[1] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 97, 1913.

[2] Ransome, F. L., Geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 123, 1909.

[3] Ransome, F. L., and Calkins, F. C., op. cit., p. 103.

[4] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 162, 1913.

[5] Ransome, F. L., and Calkins, F. C., op. cit., p. 103.

[6] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 18, 1910.

[7] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 78, 1913.

[8] Hill, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, p. 244, 1913.

[9] Bowles, O., Pyromorphite from British Columbia: Am. Jour. Sci., 4th ser., vol. 27, p. 40, 1909.

[10] Leonhard, G., Neues Jahrb., 1867, p. 449.

[11] Hill, J. M., The Grand Gulch mining region, Mohave County, Ariz.: U. S. Geol. Survey Bull. 580, p. 52, 1914.

chloride is more soluble than lead chlorophosphate. The accumulation of the chloride in the oxidized zones of lead deposits is generally limited by the amount of phosphate available in the natural solutions.

Phosgenite, $PbCO_3.PbCl_2$, another rare lead chloride, has been found with cerusite in the Terrible mine,[1] near Ilse, Custer County, Colo., where it is doubtless secondary, possibly after galena.

Beaverite, $CuO.PbO.Fe_2O_3.2SO_3.4H_2O$, is fairly abundant in oxidized ores of the San Francisco region, Utah.[2] It occurs in the Horn Silver mine, where it is found in the oxidized ores resulting from the alteration of an ore body composed principally of sulphides of lead, iron, zinc, and copper.[3] It is probably present also in the Alta district, Utah, in the Hidden Treasure mine, Ophir district, and in the Paymaster mine, in the Beaver Dam Mountains, Washington County.

Corkite, a hydrous phosphate and sulphate of lead and iron, is found in the Harrington-Hickory and Wild Bill mines, San Francisco region, and in the Star district, Utah. In both the mines named, according to Butler,[4] the original ores were replacements of limestone near an intrusive rock, and considerable apatite and contact silicates were formed with the metallic sulphides, mainly pyrite, galena, sphalerite, and chalcopyrite. The corkite is a secondary mineral resulting from the alteration of these ores, the phosphate doubtless being derived from the apatite and the metallic content from the sulphides.

Linarite, $(PbCu)SO_4.(PbCu)OH_2$, is an oxidation product of lead-copper ores but is seldom abundant. Specimens of great beauty are found in the Cerro Gordo mine, Inyo County, Cal.,[5] and fine incrustations, probably linarite, are found on cavities of oxidized ore of the Horn Silver mine, Utah.[6] It is known also at Elkhorn, Mont.[7]

A new basic lead-copper sulphate, having the formula $PbSO_4.CuSO_4.CuO$ and occurring as a dull lemon-yellow powder, was found by Lindgren in outcrops at the Sedalia mine, near Salida, Colo.[8]

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[1] Hunter, J. F., Some cerusite deposits in Custer County, Colo.: U. S. Geol. Survey Bull. 580, p. 34, 1914.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 107, 1913.

[3] Butler, B. S., Occurrence of complex and little known sulphates and sulpharsenates as ore minerals in Utah: Econ. Geology, vol. 8, p. 316, 1913. Butler, B. S., and Schaller, W. T., Some minerals from Beaver County, Utah: Am. Jour. Sci., 4th ser., vol. 32, p. 418, 1911.

[4] Butler, B. S., op. cit., Econ. Geology, vol. 8, p. 318, 1913. Butler, B. S., and Schaller, W. T., op. cit., p. 423.

[5] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 105, 1914.

[6] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 106, 1913.

[7] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 3, p. 464, 1901.

[8] Lindgren, Waldemar, Notes on copper deposits in Chaffee, Fremont, and Jefferson counties, Colo.: U. S. Geol. Survey Bull. 340, p. 164, 1908.

Plumbojarosite, $PbO.3Fe_2O_3.4SO_3.6H_2O$, is a secondary mineral found in the oxidizing zones of lead deposits,[1] especially in arid countries. Locally it is of value as an ore. Like most basic sulphates, it is probably somewhat soluble and more so than the sulphate of lead, anglesite. That it is moderately stable, however, is shown by its occurrence in Utah[2] at no less than 18 localities, including the San Francisco region,[3] the Marysvale,[4] Clifton, Fish Springs, Lucin, Ophir, and Stockton districts,[4] and at American Fork.[5] It has been identified also at Cook's Peak, N. Mex.,[6] and at the Boss gold-platinum deposit, Yellow Pine district, Nevada.[7] It probably occurs also at Leadville, Colo.[8] In many regions it has doubtless been overlooked. The color of plumbojarosite ranges from light ocher yellow to dark brown. Butler states that it may readily be distinguished from the hydrated iron oxides, for the oxides have a harsh, gritty feel when rubbed between the fingers, whereas the basic sulphates, being micaceous, have a smooth, oily feel.[9] The occurrences at Alta, Utah, and at Leadville, Colo., are in regions having a moist climate.

Leadhillite, $4PbO.SO_3.2CO_2.H_2O$, a basic sulphatocarbonate of lead, is found in ores altered by surface agencies and is probably confined to such deposits.

Bindheimite, $Pb_3Sb_2O_8+aq$, the hydrated antimonite of lead, according to Boutwell is probably a frequent oxidation product of galena-tetrahedrite ores at Park City, Utah.[10] Van Horn[11] also identified it in that district. Knopf[12] mentions bindheimite as an oxidation product of the Cerro Gordo mine, California. It is found also in Sevier County, Ark., where according to Hess[13] it is an alteration product of jamesonite. It probably occurs at the Horn Silver mine, San Francisco region, Utah.[14]

Anglesite, $PbSO_4$, is known only as an alteration product. Most commonly it forms from galena, but it has been noted also as an

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[1] Butler, B. S., Sulphates and arsenates in Utah: Econ. Geology, vol. 8, p. 311, 1913.

[2] Idem, p. 312.

[3] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 109, 1913.

[4] Butler, B. S., Econ. Geology, vol. 8, p. 315, 1913.

[5] Hillebrand, W. F., and Wright, F. E., Am. Jour. Sci., 4th ser., vol. 30, p. 191, 1910.

[6] Hillebrand, W. F., and Penfield, S. L., Am. Jour. Sci., 4th ser., vol. 14, p. 213, 1902.

[7] Knopf, Adolph; A gold-platinum-palladium lode in southern Nevada: U. S. Geol. Survey Bull. 620, p. 8, 1916.

[8] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 606, 1886.

[9] Butler, B. S., Econ. Geology, vol. 8, p. 313, 1913.

[10] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, 1912.

[11] Van Horn, F. R., The occurrence of bournonite, jamesonite, and calamine at Park City, Utah: Am. Inst. Min. Eng. Trans., vol. 49, p. 292, 1915.

[12] Knopf, Adolph, U. S. Geol. Survey Bull. 540, p. 105, 1914.

[13] Hess, F. L., The Arkansas antimony deposits: U. S. Geol. Survey Bull. 340, p. 257, 1908.

[14] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 106, 1913.

alteration product of guitermanite,[1] an arsenic sulphide of lead, and also of other minerals. According to Penrose,[2] the sulphate forms as an intermediate product when galena is altered to cerusite, and at Leadville, Colo., S. F. Emmons[3] found that thin crusts of anglesite occurred between galena and the crust of carbonate which enveloped it. Umpleby observed also that galena disseminated in quartzite in the Dome district, Idaho, alters first to anglesite and the latter to cerusite.[4] In the Yellow Pine district, Nevada, also, according to Hill,[5] galena is surrounded by anglesite, which is in turn surrounded by cerusite, and all enveloped by smithsonite. Anglesite occurs also as a band between galena and cerusite in the Texas district, Lemhi County, Idaho.[6]

At Park City, Utah, anglesite is an intermediate product between galena and cerusite, lining cavities in massive galena and forming zones one-eighth to one-fourth inch wide between galena and cerusite.[7]

In the Creede district, Colo., nodules of galena are covered with ¼-inch shells of anglesite, which are coated with cerusite.[8] (See p. 358.) Anglesite was the most important mineral of the oxidized ores of the Horn Silver mine, San Francisco district, Utah.[9] In general it was soft and earthy, but where it surrounded unaltered galena it was hard.

It is associated with carbonates and sulphide in oxidized zones of deposits at Bingham, Utah.[10] Boutwell describes an interesting specimen consisting of a kernel of galena covered with anglesite, which in turn is coated with cerusite, upon which is deposited yellow lead oxide, probably massicot. In the sideritic lead ores of the Coeur d'Alene district, Idaho, according to Ransome,[11] no anglesite has been detected, but the carbonate appears to form without the intermediate sulphate.

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[1] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colo.: U. S. Geol. Survey Bull. 182, p. 87, 1901.

[2] Penrose, R. A. F., jr., Superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 297, 1894.

[3] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 546, 1886.

[4] Umpleby, J. B., Lead-silver deposits of the Dome district, Idaho: U. S. Geol. Survey Bull. 540, p. 219, 1914.

[5] Hill, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, pp. 248, 254, 1914.

[6] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 97, 1913.

[7] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 114, 1912.

[8] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. — (in preparation).

[9] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 105, 1913.

[10] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 113, 1905.

[11] Ransome, F. L., and Calkins, F. C., op. cit., p. 132.

Anglesite is much more common than cerusite in the oxidized lead ores of Lake City, Colo.,[1] and is of considerable economic value in this district. In the upper 100 feet of the Moro vein particularly it is abundant. (See fig. 25.)

Cerusite, $PbCO_3$, is unknown as a primary mineral but is a common alteration product, particularly of galena. It frequently occurs as a heavy sand, called by miners "sand carbonate." Butler states that cerusite-bearing limonite in certain deposits in Utah may be detected when the material is crushed in the hand, the crunching sound enabling one familiar with the deposits to separate ore from waste.[2]

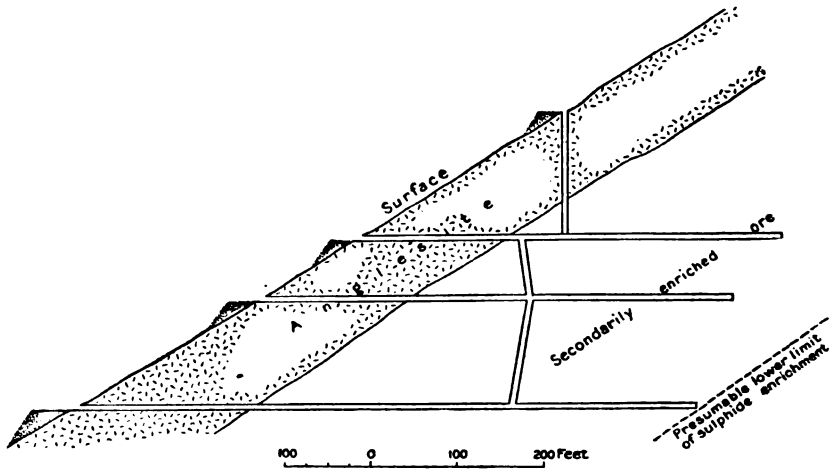

FIGURE 25.—Longitudinal section of the Moro mine, Lake City, Colo., showing depth of anglesite alteration. After J. D. Irving and Howland Bancroft.

Cerusite was abundant in the upper levels of the mines at Bingham, Utah,[3] where it was generally associated with anglesite and galena. At Park City, Utah,[4] also, it was common in the upper levels and in the Mammoth stope of the Silver King mine is extended downward below the 900-foot level; and in the "Gash" lode of this mine it was found at a depth of 1,100 feet. It usually occurs in crevices or pits in galena, which are lined with a thin coating of anglesite that is covered by a velvet-like layer of minute tabular crystals of cerusite.

In the San Francisco region, Utah, cerusite is the most valuable secondary lead ore. It is generally mixed with limonite, but some of the ore bodies are nearly pure. At Creede, Colo.,[5] it is an important

[1] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, p. 61, 1911.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 100, 1913.

[3] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 226, 1905.

[4] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 111, 1913.

[5] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. — (in preparation).

mineral, as it is also at Leadville.[1] There great masses of ore are practically pure lead carbonate.[2] Though present it is not abundant at Philipsburg, Mont.[3] It is abundant in the upper parts of some veins of the Coeur d'Alene district, Idaho.[4]

Cerusite replaces scalenohedra of calcite at Granby, Mo.[5] A valuable deposit in which cerusite is essentially the only ore mineral is found at the Terrible mine, near Ilse, Custer County, Colo. A great mass of this ore, extending to considerable depth and worth more than half a million dollars, was found in shattered granite. No galena nuclei have been found in the ore, and S. F. Emmons[6] suggested that the deposit was formed by ascending carbonated waters. Hunter,[7] who has recently studied the region, considers it more probable that the deposit is a surface alteration of galena. Cerusite is an important mineral at Cerro Gordo, Cal.,[8] and is the principal ore mineral in the Texas and Spring Mountain districts, Lemhi County, Idaho.[9]

Cerusite is most abundant in deposits where the country rock is limestone, although it is not limited to such deposits. Very commonly the carbonate replaces galena metasomatically. According to Penrose[10] lead sulphate may form intermediately between the sulphide and carbonate. (See p. 363.) Its formation is favored by the low solubility of the carbonate. In the Coeur d'Alene district the change is not everywhere a metasomatic replacement for, according to Ransome,[11] cerusite is common in little vugs or crevices in the sulphides, where it is formed on unaltered galena by solutions that have percolated downward from the oxidized zone. As stated by Ransome, the oxidation of siderite may supply carbonate for cerusite. Because of its low solubility,[12] lead carbonate is relatively stable.

Mineral syntheses of cerusite crystals are numerous. They are produced where alkali or alkaline earth carbonates react slowly with

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[1] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 546, 1886.

[2] Ricketts, L. D., The ores of Leadville, p. 33, Princeton, 1883.

[3] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 157, 1913.

[4] Ransome, F. L., and Calkins, F. C., op. cit., p. 92. Rogers, A. F., Am. Philos. Soc. Proc., vol. 49, p. 18, 1910.

[5] Rogers, A. F., op. cit., p. 19.

[6] Emmons, S. F., The mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, pp. 468–469, 1896.

[7] Hunter, J. F., Some cerusite deposits of Custer County, Colo.: U. S. Geol. Survey Bull. 580, p. 35, 1914.

[8] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 105, 1914.

[9] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 78, 1913.

[10] Penrose, R. A. F., Superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 297, 1894.

[11] Ransome, F. L., and Calkins, F. C., op. cit., p. 112.

[12] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

lead.[1] Cerusite was found by A. F. Rogers on Chinese copper coins of the Kang dynasty, of the seventh century, recently exhumed.[2]

Hinsdalite, $2PbO.3Al_2O_3.2SO_3.P_2O_5.6H_2O$, in the Golden Fleece mine,[3] Lake City, Colo., is an important ore of lead. It is found in veins in rhyolite associated with quartz, barite, pyrite, galena, tetrahedrite, and rhodochrosite. As it is a hydrous sulphate containing phosphorus, it is presumably formed near the surface or in the zone of oxidation, but whether by ascending or superficial waters is uncertain.

Bournonite, $PbCuSbS_3$, is easily confused with tetrahedrite, which it closely resembles. Van Horn[4] described crystallized specimens from Park City, Utah, obtained from the 1,300-foot level and presumably primary. It is associated with tetrahedrite in some veins in the Bradshaw Mountains, Ariz.,[5] and it is sparingly scattered through quartzose ores of the Elkhorn mine, Montana.[6]

Jamesonite, $Pb_2Sb_2S_5$, a sulphantimonite of lead nearly related to stibnite, is a comparatively rare mineral but occurs in considerable abundance near Zimapan, Mexico, where it is associated with albite, pyrrhotite, and sphalerite, in a deposit that has replaced limestone at considerable depths.[7] It is found also in deep levels in the Silver King Coalition mine, Park City, Utah.[8] In Star Canyon, Humboldt County, Nev.,[9] argentiferous jamesonite is associated with galena and tetrahedrite in quartz. It occurs also in Eureka and Esmeralda counties. It is associated with galena and tetrahedrite in ores of the Bassick[10] mine, Custer County, Colo. In the Bradshaw Mountains, Yavapai County, Ariz., it carries free gold.[11] I have no knowledge of jamesonite formed by processes of superficial alteration.

Galena, PbS, is a "persistent" mineral—a mineral formed under many natural conditions. The most important deposits of galena in

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[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 679, 1916.

[2] Rogers, A. F., Minerals observed on buried Chinese coins of the seventh century: Am. Geologist, vol. 31, p. 45, 1903.

[3] Larsen, E. S., jr., and Schaller, W. T., Hinsdalite, a new mineral: Am. Jour. Sci., 4th ser., vol. 32, p. 251, 1911.

[4] Van Horn, F. B., The occurrence of bournonite, jamesonite, and calamine at Park City, Utah: Am. Inst. Min. Eng. Trans., vol. 49, p. 292, 1915.

[5] Jaggar, T. A., jr., and Palache, Charles, The Bradshaw Mountains quadrangle: U. S. Geol. Survey Geol. Atlas, Bradshaw Mountains folio (No. 126), p. 10, 1905.

[6] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 459, 1901.

[7] Lindgren, Waldemar, and Whitehead, W. L., A deposit of jamesonite near Zimapan, Mexico: Econ. Geology, vol. 9, p. 435, 1914.

[8] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 187, 1912. Van Horn, F. R., op. cit., p. 296.

[9] Ransome, F. L., Notes on some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 67, 1909.

[10] Emmons, S. F., Mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 432, 1896.

[11] Jaggar, T. A., jr., and Palache, Charles, op. cit., p. 9.

the United States are the disseminated ores of southeastern Missouri and the lead-silver ores of the Coeur d'Alene district, Idaho.[1] The galena in Missouri is nearly pure lead sulphide, has a perfect cleavage, and is generally in cubic crystals; the galena of the Coeur d'Alene district contains appreciable silver, is generally not so well crystallized, and has a much less perfect cleavage, so that a freshly broken fracture resembles that of steel and the mineral is called "steel galena" by the miners. Some antimonial galena has a similar fracture. At Park City, Utah,[2] the galena in replaced limestone beds, which constitutes the bonanzas of the district, is generally massive, whereas that in fissures is generally crystallized. Some galena is rich in silver, which is present as argentite. Nissen and Hoyt[3] showed that minute crystals of the silver sulphide are rather evenly spaced through massive lead sulphide, even when only a little silver is present, and melts of mixtures containing 0.2 per cent or more silver sulphide solidified as the two sulphides and not as an isomorphous compound.

A noteworthy feature of galena is the occurrence of minute quantities of a manganese sulphide[4] in many specimens.

The stability of galena in the oxidized zone has already been mentioned. The relative insolubility of galena in natural waters is shown by the experiments of Buehler and Gottschalk (p. 109) and is confirmed abundantly by observations in the oxidized zones of deposits. Galena is commonly found in sluice boxes of placer mines, and it is plowed up in the fields of the southwestern Wisconsin zinc district. Even in districts where the climate is comparatively moist, such as the Breckenridge[5] and Coeur d'Alene[6] districts, galena is found at the very outcrops of some ore veins.

At the Elkhorn mine, near Ketchum, Idaho, galena partly oxidized to cerusite collected in a shallow sag, forming a sort of placer, and was shoveled up and jigged.[7]

In the Coeur d'Alene district, according to Ransome and Calkins,[6] there is little evidence of enrichment of either silver or lead by cold solutions. In the Breckenridge district[5] the characteristic ore of

[1] Ransome, F. L., and Calkins, F. C., op. cit., p. 112.

[2] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 106, 1913.

[3] Nissen, Arvid, and Hoyt, C., Occurrence of silver in argentiferous galena ores: Econ. Geology, vol. 10, p. 172, 1915.

[4] Nishihara, G. S., The rate of reduction of acidity of descending waters by certain ore and gangue minerals and its bearing upon secondary sulphide enrichment: Econ. Geology, vol. 9, p. 747, 1914.

[5] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 166, 1911.

[6] Ransome, F. L., and Calkins, F. C., op. cit., p. 133.

[7] Lindgren, Waldemar, The gold and silver veins of Silver City, De Lamar, and other mining districts in Idaho: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 210, 1900.

the upper levels is argentiferous galena, more or less altered to cerusite, whereas in the lower levels sphalerite and pyrite become increasingly abundant, suggesting enrichment in the upper levels by addition of lead or by subtraction of zinc, or by both.

At Leadville, Colo., according to Blow,[1] stringers of galena rich in silver penetrate the limestone below the bodies of carbonate ores. As noted by Vogt,[2] and also by Finlayson,[3] the pyritic ore of the Rio Tinto mine in Spain is cracked and is generally seamed with deposits of chalcocite, bornite, chalcopyrite, and galena, and the galena, according to Finlayson, is commonly of most recent formation. It is not stated, however, that the galena was deposited by descending waters.

Weed[4] has described secondary galena from the sulphide zone at Neihart, Mont., where it is associated with zinc blende and incrusted with polybasite; and Irving and Bancroft[5] state that some of the galenā of the Lake City district, Colorado, is without doubt connected genetically with oxidation processes. In that district a gray coating of a lead compound, thought to be galena, occurs in cracks of shattered sphalerite and covers its exposed surfaces. Possibly the gray sphalerite observed in many deposits of the West owes its color to such a veneer of galena. Galena has replaced sphalerite in the Horn Silver mine, San Francisco district, Utah.[6]

A survey of the occurrences of lead deposits for examples giving evidence of considerable secondary precipitation of lead sulphide in lode ores has not been very fruitful of results. On the other hand, there is much evidence of migration of lead in cold carbonated solutions and of its precipitation as sulphide in the important lead and zinc ores of the Mississippi Valley. These processes, as already stated, do not come within the scope of this investigation.

LEAD-BEARING DEPOSITS.[7]

SOUTHEASTERN MISSOURI LEAD DISTRICT.

The disseminated lead deposits of southeastern Missouri are in St. Francois and adjoining counties, 50 miles south of St. Louis.

[1] Blow, A. A., The ore chutes and recent developments of Iron Hill, Leadville, Colo.: Am. Inst. Min. Eng. Trans., vol. 18, p. 169, 1890.

[2] Vogt, J. H. L., Das Huelva-Kiesfeld: Zeitschr. prakt. Geologie, vol. 7, p. 249, 1899.

[3] Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, p. 421, 1910.

[4] Weed, W. H., The enrichment of gold and silver veins, in Pošepný, Franz, The genesis of ore deposits, p. 485, 1902.

[5] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, p. 97, 1911.

[6] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[7] Other lead deposits have been described on pp. 280–304.

The district[1] is in an area of sedimentary rocks, of which a geologic section, after E. R. Buckley, is given below:

	Feet.
Cambrian:	
Potosi dolomite	300+
Doe Run argillaceous dolomite	60–100
Derby dolomite	40
Davis formation: Shale, limestone, limestone conglomerate	170
Bonneterre: Magnesian limestone, sandy dolomite, and shale (principal ore-bearing formation)	365±
Lamotte sandstone	200±
Unconformity.	
Pre-Cambrian:	
Granite and rhyolite with intruding diabase dikes.	

The sedimentary beds, though generally flat, dip locally as much as 45°. They are cut by faults which strike northwest or northeast. Normal faults prevail, and single faults have vertical slips of less than 100 feet, but some fault zones have throws measuring 700 feet. A little ore is found in the Potosi limestone, but more in the Bonneterre limestone, particularly near its base. Some galena occurs also in the Lamotte sandstone and in pre-Cambrian rocks, but from the pre-Cambrian lead has not been mined successfully. The ore occurs as crystals and masses of galena disseminated in limestone or shale, as horizontal sheets along the bedding, in small cavities or filling the small joints, and in shale and clay along faults. One ore body was 9,000 feet long, 25 to 500 feet wide, and 5 to 100 feet thick.

The limestone contains considerable organic matter and chlorite. The minerals of the deposits are galena, a little pyrite, and at some places a little chalcopyrite and sphalerite. The lead carries only about 2 ounces of silver to the ton of concentrates. At Mine Lamotte and Fredericktown cobalt and nickel sulphide are found, and these metals were once extracted in small quantities. Winslow names pyrrhotite as an associate of the ores, but Buckley does not mention it. Barite is associated with the ores in the Potosi limestone.

Both Buckley and Winslow attribute the metallization to ground water. The lead was formerly widely dispersed in the Bonneterre and probably in other formations. It was dissolved in the zone of oxidation and concentrated in fractures through which the solutions moved, being precipitated on contact with reducing agents in beds of limestone or associated shale. Buckley thinks that the solutions were in part descending and in part ascending waters. Numerous samples of mine water collected by him proved to be moderately

[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties, Mo.: Missouri Bur. Geology and Mines, vol. 9, pts. 1 and 2, 1909; in Bain, H. F., and others, Types of ore deposits, pp. 110–130, San Francisco, 1911. Winslow, Arthur, Missouri Geol. Survey, vols. 6 and 7, 1894; U. S. Geol. Survey Bull. 132 1896. Keyes, C. R., Missouri Geol. Survey, vol. 9, 1896.

strong solutions of alkalies and alkali earths, mixed waters of the carbonates, sulphates, and chlorides. Some carry as much as 15 parts per million of lead sulphate.

Buckley[1] has noted the presence of basic igneous rocks at two places in St. Genevieve County, which adjoins the ore-bearing region on the east. These appear to be intrusive in the lower part of the Bonneterre limestone and carry visible galena and sphalerite. The bulk of the evidence, however, points to cold solutions as metallizing agents.

COEUR D'ALENE DISTRICT, IDAHO (LEAD-SILVER DEPOSITS).

The geology and ore deposits of the Coeur d'Alene mining district, Idaho, are described by Ransome and Calkins.[2] The district is in an area of pre-Cambrian quartzite and siliceous slates, which are intruded by large masses of monzonite and related rocks. Some contact metamorphism has taken place and certain of the ore bodies are of the garnet-sulphide type, but the principal deposits are wide lead-silver lodes free from garnet.

This country is extensively faulted, but the lodes are not along the major faults. The ores were formed partly by filling open spaces but largely by replacement along zones of fissuring or shearing. The deposits, which have a vertical range of 4,000 feet, were probably formed under several thousand feet of rock which has since been removed.

The ore minerals are galena, pyrite, chalcopyrite, sphalerite, and subordinate pyrrhotite, with some argentiferous tetrahedrite and stibnite. Siderite is the most abundant gangue mineral, with subordinate quartz and a little barite. The ores carry about 8 per cent lead and 4 ounces of silver to the ton.

Ransome[3] says:

> Although the mineralogical character of the large lead-silver deposits exhibits great uniformity, some of the ore bodies are known to change their composition with increase of depth. No evidence has been found, however, that in any way connects the observed changes with the descent of solutions from the zone of oxidation. Such variations as occur are apparently original and not due to secondary enrichment from above.
>
> In the process of oxidation cerusite develops from galena without any visible intermediate product. The change is not a direct replacement of the sulphur by carbonic anhydride, but the galena is irregularly corroded by the oxidizing

[1] Buckley, E. R., in Bain, H. F., and others, Types of ore deposits, p. 105, San Francisco, 1911.

[2] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, 1908. Pardee, J. T., Geology and mineralization of the upper St. Joe Basin, Idaho: U. S. Geol. Survey Bull. 470, pp. 39–61, 1911. Calkins, F. C., and Jones, E. L., jr., Geology of the St. Joe-Clearwater region, Idaho: U. S. Geol. Survey Bull. 530, pp. 75–86, 1913. Hershey, O. H., Genesis of the silver-lead ores of the Wardner district, Idaho: Min. and Sci. Press, vol. 104, pp. 750–753, 786–790, 825–827, 1912.

[3] Ransome, F. L., and Calkins, F. C., op. cit., p. 112.

solutions and cerusite crystals are deposited in the cavities thus formed. In other words, the lead itself is somewhat mobile during the change from sulphide to carbonate. The various minerals of the oxidized ores are still forming and make up soft earthy masses in which no sequence of crystallization is apparent. It is not known, for example, whether pyromorphite, like cerusite, forms directly from galena or whether it is derived from some oxysalt of lead.

The small quantity of sphalerite formerly in the ores which have undergone oxidation has left no recognizable trace of its presence.

In the Caledonia mine, more recently developed, secondary tetrahedrite appears to have formed on a somewhat extensive scale.[1] The deposit is a vein in quartzite and carries lead, silver, and copper. Although the mine is developed by a deep tunnel, the ore is said to have come mainly from above the 500-foot level. The upper parts of the ore shoots contain cerusite, marcasite, and pyromorphite, with limonite and manganese compounds, cuprite, and copper carbonates. Native silver was locally abundant. In places the ore showed small cores of tetrahedrite surrounded by concentric zones of cuprite, malachite, and azurite.[2] With increase of depth galena and chalcopyrite become more abundant. Siderite is less abundant than in other mines of the region and tetrahedrite, which is highly argentiferous, is more abundant. It lines and fills cracks in chalcopyrite. Argentiferous covellite with silver in a form not determined fills cracks and forms crusts on galena. Such coatings, fairly compact and of sooty appearance, range in thickness from one-sixteenth of an inch to 6 inches.

LEAD DEPOSITS OF CUSTER COUNTY, COLORADO.

A large lead deposit is located near Ilse,[3] about 12 miles northeast of Silver Cliff, Custer County. Estimates of the total production of the district range from $500,000 to over $1,000,000 worth of lead, the larger part of which has come from the Terrible mine. The principal rock in the region is granite, generally gneissoid, which is intruded by dikes and small bodies of syenite, diorite, and pyroxenite.[4]

The deposits are chiefly localized along zones of faulting and crushing in the granite and granite gneiss. The crushed zone in which the Terrible mine is localized can be traced 2 miles or more. It shows a notable amount of crushing, with slickensided surfaces in numerous places, and is characterized by gouge, clay selvage, and alteration, all of which indicates a zone of faulting.[5]

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[1] Shannon, E. V., Secondary enrichment in the Caledonia mine, Coeur d'Alene district, Idaho: Econ. Geology, vol. 8, p. 565, 1913.

[2] Shannon, E. V., op. cit., p. 566.

[3] Hunter, J. F., Some cerusite deposits in Custer County, Colo.: U. S. Geol. Survey Bull. 580, pp. 24–37, 1915. Emmons, S. F., The mines of Custer County, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, pp. 468–469, 1896. A curious deposit of cerusite in Colorado: Eng. and Min. Jour., vol. 83, pp. 844–845, May 4, 1907.

[4] Hunter, J. F., op. cit., p. 27.

[5] Idem, p. 31.

In the open cut at the Terrible mine the ore zone consists of about 75 feet of crushed, altered, and iron-stained granite and granite gneiss with bodies of cerusite. On the hanging wall the pay zone is bordered by about 15 feet of clay gouge with brecciated fragments of altered granitic material. Beyond and parallel to the gouge there is a dikelike body of diorite. The clay gouge and diorite are barren.

Cerusite is practically the only ore mineral, though phosgenite also is present. Extensive leaching and alteration is indicated by the honeycombed structure and by the abundant limonite and other oxides. Although the mine has been worked to the 250-foot level, it is said that no sulphides have appeared. S. F. Emmons[1] regarded the deposit as probably formed through the agency of ascending carbonate waters, but Hunter[2] believes that they have formed through the oxidation of sulphides and points to the occurrence of galena near by.

ZINC.

PRINCIPAL ZINC MINERALS.

The chemical composition of the principal zinc minerals is shown below:

Goslarite $ZnSO_4.7H_2O$.
Smithsonite $ZnCO_3$.
Monheimite $(Zn,Fe)CO_3$.
Calamine $Zn_2H_2SiO_5$ or $2ZnO.SiO_2.H_2O$.
Willemite Zn_2SiO_4.
Hopeite $Zn_3P_2O_8.4H_2O$.
Hydrozincite $ZnCO_3.2ZnO_2H_2$ or $3ZnO.CO_2.2H_2O$.
Aurichalcite $2(Zn,Cu)CO_3.3(Zn,Cu)O_2H_2$.
Wurtzite ZnS.
Sphalerite ZnS.

SOLUBILITIES OF ZINC COMPOUNDS.

The solubilities of several zinc salts determined by Kohlrausch are stated below:

$ZnSO_4$.	$ZnCl_2$.	$ZnCO_3$.	$Zn(NO_3)_2$.
531.2 3.1	2,039 9.2	0.04 ? a.0003?	1,178 4.7

a R. C. Wells gives 0.00017. (See U. S. Geol. Survey Bull. 540, p. 107.)

The upper number in each column shows the number of grams of the anhydrous salt held in solution in a liter of water at 18° C.; the lower number shows the molar solubility or the number of mols contained in a liter of the saturated solution.

[1] Cited in U. S. Geol. Survey Bull. 580, p. 25, 1915. [2] Hunter, J. F., op. cit.,

NATURE AND RELATIONS OF ZINC MINERALS.

Zinc is bivalent in all its compounds. The sulphate and the chloride are very soluble and the carbonate is more soluble than carbonate of lead. A liter of pure water dissolves at ordinary temperature and pressure 0.0000706 mol of freshly precipitated zinc sulphide. (See p. 117.) The principal primary zinc mineral is the isometric form of the sulphide, sphalerite. Wurtzite, the hexagonal form of the sulphide, is comparatively rare. In some deposits the primary zinc minerals are oxides, such as franklinite, zincite, and gahnite, but these are rare or absent in sulphide deposits.

In sulphide deposits zinc sulphide is dissolved by sulphuric acid generated by oxidation of iron pyrite and other iron sulphides, and more readily in the presence of ferric sulphate. In deposits free from pyrite, sphalerite oxidizes more slowly.

As zinc sulphide is easily dissolved in sulphuric acid sphalerite would not form in a highly acid solution. If, through reactions with the wall rock, the solution should become feebly acid or neutral, then zinc sulphide could be precipitated. Allen and Crenshaw[1] state that sphalerite is precipitated from acid as well as from alkaline solutions, but that wurtzite is precipitated only from acid solutions and is probably always secondary. As zinc sulphide is one of the most soluble of the common sulphides it could not replace sulphides of copper, silver, or lead. Possibly it could replace pyrite, marcasite, or pyrrhotite under certain conditions, but no examples of its pseudomorphs after these minerals are known to me. It is itself replaced by chalcocite and covellite and probably by argentite and galena.

There is every reason to suppose that zinc sulphide in carbonate rocks in the zinc deposits of the upper Mississippi Valley in southwestern Wisconsin has been dissolved by underground waters and has been reprecipitated as sulphide in large amounts where the solutions were in contact with carbonaceous material.

In view of the moderately high solubility of its sulphide zinc might be dissolved as zinc sulphide as well as zinc sulphate, but its solution as sulphide is relatively slow. The chloride is even more soluble than the sulphate and its solid phase is unknown in ore deposits.

Secondary zinc blende has been found in western ore deposits in rocks other than limestone, but so far as the records show its occurrence in western deposits is exceedingly rare. Large quantities of zinc are undoubtedly dissolved from the outcrops and oxidized zones of deposits in which it occurs as sulphide and are transported as sulphate downward, below the water level. To account for its disposition is one of the most perplexing problems in the study of mineral genesis.

[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: Am. Jour. Sci., 4th ser., vol. 34, p. 359, 1912.

Doubtless much of it escapes to the surface and is scattered, yet many analyses of waters issuing from zinc deposits show much less zinc than would be expected. In two alkaline waters from sphaleritic deposits of Creede, Colo., no zinc is reported. In waters from several other deposits it is present in considerable amounts, but the quantity of zinc found in some of these is small. In waters from several deposits at Ducktown, Tenn., the zinc in solution is less than the copper, although the sulphide deposits contain as much zinc as copper and copper is now being precipitated. Some sludges deposited by mine waters where they issue to the air contain considerable zinc; others contain practically none. Zinc salts do not hydrolyze so readily as ferric salts when exposed to air. With carbon dioxide they form smithsonite, hydrozincite, and aurichalcite, but these compounds are generally less abundant in outcrops than hydrous iron oxide. The oxide of zinc is almost universally primary, but an oxidized form, an unnamed species, is said to be formed by processes of superficial alteration. W. H. Hobbs[1] described an occurrence of white zinc oxide from Highland, Wis., which forms a botryoidal coating at the surface.

OXIDATION OF PYRITE-GALENA-SPHALERITE ORE BODIES IN LIMESTONE.

In limestone a solution of zinc sulphate precipitates zinc carbonate ores. These ores have lately become prominent, particularly in several districts of western America, where superficial changes have produced notable concentration of zinc. These processes have recently been discussed by Butler,[2] Knopf,[3] and Loughlin.[4]

A common type of ore in limestone consists of pyrite, argentiferous galena, sphalerite, a little chalcopyrite, and other sulphides in a gangue of quartz. The ore bodies, like many deposits in limestone, are commonly large irregular masses. In the oxidation of such a deposit the lead and much of the silver remain essentially in place, the galena being in part oxidized to anglesite and cerusite. The oxidation of pyrite and sphalerite yields acid, and zinc and iron sulphates, which are carried out of the deposits in great quantities. A part of the iron remains behind as oxide, but in some deposits practically all the zinc is removed. When the solution, which is doubtless acid and carries ferric, ferrous, and zinc sulphates, moving along a water channel, encounters the limestone that surrounds the ore body, it will precipitate iron and zinc. The ferric sulphate attacks the

[1] Hobbs, W. H., Contributions from the mineralogical laboratory of the University of Wisconsin: Am. Geologist, vol. 36, p. 180, 1905.

[2] Butler, G. M., Some recent developments at Leadville: Econ. Geology, vol. 8, p. 1, 1913.

[3] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 97, 1914.

[4] Loughlin, G. F., The oxidized zinc ores of Tintic district, Utah: Econ. Geology, vol. 9, p. 1, 1914.

limestone more vigorously than ferrous sulphate and zinc sulphate, and the first material to be deposited is ferric hydroxide.

$$\underset{\text{(Ferric sulphate.)}}{2Fe_2(SO_4)_3}+\underset{\text{(Limestone.)}}{6CaCO_3}+21H_2O=$$
$$\underset{\text{(Limonite.)}}{2Fe_2O_3.3H_2O}+6\underset{\text{(Gypsum.)}}{(CaSO_4.2H_2O)}+6H_2CO_3.$$

Thus limonite is found near the ore body and with it is commonly associated a little gypsum, which, however, being somewhat soluble, is only moderately stable, and is in large part carried away by the underground waters. The solution which is moving farther into the limestone still contains ferrous sulphate and zinc sulphate, for ferric sulphate attacks limestone more vigorously than zinc sulphate. Ferrous iron and zinc are precipitated by calcite more slowly than ferric iron. At Leadville, at Tintic, and at Cerro Gordo ferric oxide generally lies a little nearer the original ore body than zinc carbonate. With ferrous salt the reaction with limestone would be:

$$FeSO_4+CaCO_3+2H_2O=CaSO_4.2H_2O+FeCO_3.$$

With zinc sulphate it would be:

$$ZnSO_4+CaCO_3+2H_2O=CaSO_4.2H_2O+ZnCO_3.$$

Under some conditions a zinc-iron carbonate or sideritic smithsonite, monheimite, is formed. This reaction has recently been investigated by Wells.[1] Dilute solutions of two metallic salts in equivalent (molar) quantities were precipitated with only enough sodium carbonate for one metal. With equivalent quantities of zinc and calcium nearly all the zinc and only a trace of calcium is precipitated. With equivalent quantities of iron and calcium, nearly all the iron and only a trace of calcium is precipitated. With iron and zinc a little more iron than zinc is precipitated. The solubilities of iron and zinc carbonates[2] in gram equivalents per liter are, respectively, 0.000062 and 0.000170. The acid carbonate of calcium is highly soluble. That the solutions would carry an excess of carbon dioxide is indicated by the reaction forming limonite as stated above, where carbon dioxide is set free. Sideritic smithsonite, or monheimite, contains iron carbonate in varying proportions. Some smithsonite is nearly pure and some contains as much as 20 per cent of iron carbonate, or even more. Deposits rich in iron pyrite should supply more highly ferruginous waters, and the carbonate precipitated from such waters should contain more iron.

After it is formed the smithsonite, or monheimite, with the progress of the erosion of the country, is exposed to more highly oxygen-

[1] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911. See also this paper, p. 126.

[2] Wells, R. C., as cited by Knopf, Adolph, op. cit., p. 107.

ated waters. The iron carbonate then oxidizes and stains the ore brown so that it may be easily mistaken for iron-stained limestone. Thus deposits of this character, though exposed in underground workings, have been overlooked for years.

At Tintic, Utah, according to Loughlin, the carbonate ore commonly shows the following paragenesis: The massive smithsonite, or monheimite, is covered by drusy or fibrous smithsonite, which in turn is covered by hydrozincite and by aurichalcite and calamine. With these minerals calcium carbonate and gypsum are deposited. The minerals form on the zinc carbonate by its oxidation at some places,

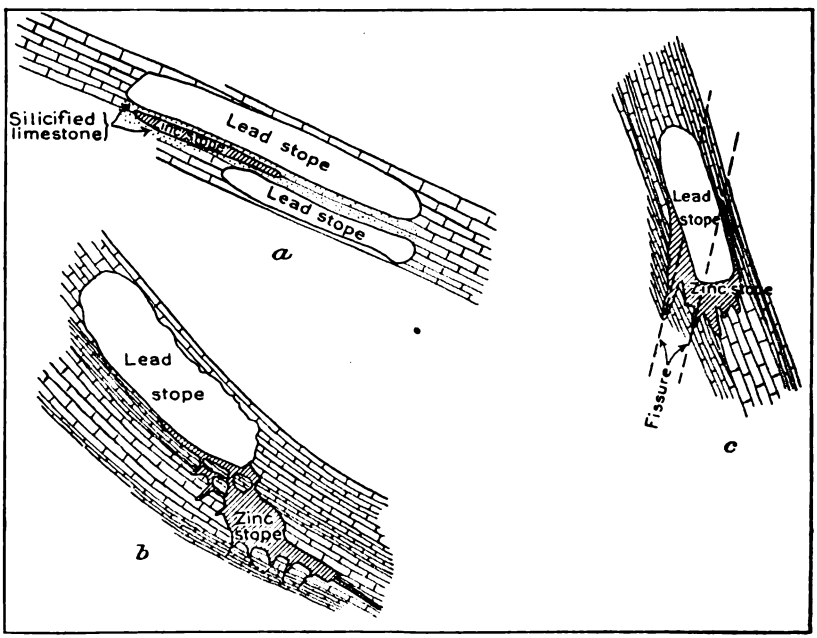

FIGURE 26.—Diagrammatic cross sections showing relations of oxidized lead ores and zinc carbonate ores at Tintic, Utah. *a*, Yankee mine; *b*, May Day mine; *c*, Gemini and Ridge and Valley mines. After G. F. Loughlin.

probably by the encroachment of more highly oxygenated waters as the country is eroded. Throughout the processes iron and manganese oxides may be deposited.

In some of the primary deposits from which the zinc ores were derived there remains little more than a trace of zinc. At Tintic, Utah, and at Cerro Gordo, Cal., the quantity of sphalerite in the lead ores, about which the smithsonite forms, is very small.

Certain structural features of these deposits should be mentioned. As shown by figure 26 they are not to be regarded as envelopes of zinc around the older lead ores, for they are seldom continuously developed, but make out on fractures, bedding planes, or wherever

watercourses are available. In some deposits they extend 100 feet or more from the original ore bodies.

OCCURRENCE OF ZINC MINERALS.

Goslarite, $ZnSO_4.7H_2O$, occurs on the walls of some mine workings as a white filiform or mosslike efflorescence, which soon disintegrates to powder when disturbed. Owing to the high solubility of zinc sulphate in water, goslarite is comparatively rare in most districts, though it is abundant in some, as at Creede, Colo.,[1] in the San Francisco region, Utah, and at Butte, Mont. In the Horn Silver mine, Utah, according to Butler,[2] considerable goslarite was found on the eleventh level, where it has been deposited by evaporation. At Butte, according to Weed,[3] zinc sulphate is carried by the moisture of the air circulating in mine openings.

Smithsonite, $ZnCO_3$, is commonly formed in the oxidized zones of zinc-bearing veins. It is most abundant in deposits in limestone. It has not been reported as a primary mineral in deposits formed by hot ascending waters. Where zinc sulphate waters attack limestone, smithsonite is deposited, calcium sulphate, the more soluble salt, going into solution. The reaction may be stated as follows:

$$ZnSO_4+CaCO_3+2H_2O=CaSO_4.2H_2O+ZnCO_3.$$

The calcium sulphate if precipitated as gypsum may remain with smithsonite or it may be carried away in solution, since it is fairly soluble in cold water (2.0 grams in a liter at 18° C.).

In the laboratory this reaction goes on very slowly. Even if sulphuric acid is added no action is at once noticeable. Presumably a film of calcium sulphate covers the calcite, retarding solution, but if a grain of common salt is added action at once becomes vigorous. The reaction product is then calcium chloride, which is very soluble compared with calcium sulphate. If more time is allowed, however, the carbonate will form according to the reaction written above. After 26 months, with a little acid in solution, the calcite is largely changed to sulphate. With acid carbonates also zinc sulphate forms smithsonite.

With its common associate, monheimite, smithsonite, as stated above, forms valuable secondary zinc deposits in limestone wall rock surrounding partly oxidized lead ore, as at Tintic, Utah; Leadville, Colo.; Kelly mine, New Mexico; Cerro Gordo, Cal., and doubtless in

[1] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. — (in preparation).

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 108, 1913.

[3] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 99, 1912.

other districts. According to Rogers,[1] smithsonite replaces crystals of both calcite and dolomite at Granby, Mo.

In the absence of pyrite or other iron sulphides, sphalerite alters directly to carbonate, but this reaction is exceedingly slow. In the sphalerite deposits near Knoxville, Tenn., which carry very little pyrite, it is said that the sulphides and a little carbonate are found practically at the outcrops.

Monheimite is zinc carbonate containing iron carbonate. It is rarely well crystallized, and although probably very common it is not reported from many districts. At Leadville, Colo.;[2] Tintic, Utah;[3] and Kelly, N. Mex.,[4] it is common. Some specimens are yellowish brown, resembling iron-stained calcite or limestone. Not all monheimite, however, is in limestone. In the F. M. D. mine, near Evergreen, Jefferson County, Colo., fractures in an amphibolite schist are coated by secondary pyrite and small aggregates of rhombohedral monheimite.[5]

Calamine, $Zn_2H_2SiO_5$, is commonly associated with smithsonite in the oxidized zones of zinciferous ores. It is not known as a primary mineral of ore veins deposited from hot solutions. At Tintic, Utah,[6] calamine is found in druses lining or filling openings in smithsonite, in limestone, or in leached material stained with iron and manganese. It also impregnates massive smithsonite and limestone and is found in layers or beds alternating with smithsonite and parallel to bedding planes, obviously a replacement of limestone. More rarely, also, at Tintic it replaces smithsonite. At Granby, Mo., calamine replaces scalenohedra of calcite.[7] It is found in oxidized ores in the Horn Silver mine, Utah,[8] and in the Cedar-Talisman mine in the same district, where it is associated with smithsonite. At Yellow Pine, Nev.,[9] it occurs as crystals lining cavities and along watercourses, and in seams between laminæ of smithsonite. In Lemhi County, Idaho,[10] calamine needles and sheaf-like aggregates, usually set on a base of smithsonite, protrude from walls of small cavities in lead-silver ore.

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[1] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 18, 1910.

[2] Butler, G. M., Some recent developments at Leadville: Econ. Geology, vol. 8, p. 3, 1913.

[3] Loughlin, G. F., The oxidized zinc ores of the Tintic district, Utah: Econ. Geology, vol. 9, p. 2, 1914.

[4] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 253, 1910.

[5] Lindgren, Waldemar, Notes on copper deposits in Chaffee, Fremont, and Jefferson counties, Colo.: U. S. Geol. Survey Bull. 340, p. 169, 1908.

[6] Loughlin, G. F., op. cit., p. 4.

[7] Rogers, A. F., op. cit., p. 19.

[8] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 102, 1913.

[9] Hill, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, p. 244, 1914.

[10] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, pp. 64, 75, 1913.

Willemite, Zn_2SiO_4, the anhydrous silicate, is much less common than calamine. It is abundant in the primary ores of Franklin Furnace, N. J.,[1] but is not reported as occurring in the secondary ores of many zinc deposits. It is noted as an alteration product, however, at Morenci, Ariz.,[2] and appears in considerable quantities at Tres Hermanas, N. Mex.,[3] where it is probably derived from zinc blende by oxidation.

Hopeite, a zinc phosphate, probably $Zn_3P_2O_8+4H_2O$, unlike the chlorphosphate of lead, pyromorphite, is rare. It was first identified in a zinc mine at Altenberg, Moresnet, between Liege and Aachen, but it is not abundant there. In two Broken Hill mines, northwestern Rhodesia,[4] it appears in quantity. It is found in a cave in an outcrop of ore that rises conspicuously above the surrounding country, which is an area of limestone and other sedimentary rocks. In this cave there are large quantities of bone breccia, with implements of early man. The bright, colorless, transparent crystals of hopeite are associated with vanadinite and calamine and are found coating bones and inside of bones and teeth. Some masses with little or no bony material weigh several pounds. In a neighboring deposit other associated materials are tarbuttite ($Zn_2(OH)PO_4$), calamine, cerusite, limonite, quartz, wad, pyromorphite, galena, and zinc blende. Doubtless hopeite was formed in this region by the reaction of phosphoric acid with a soluble zinc salt. Hopeite has been formed synthetically by precipitation from a solution of zinc phosphate in acetic acid.[5]

Hydrozincite.—The hydrous form of smithsonite, hydrozincite, $ZnCO_3.2Zn(OH)_2$, is always secondary. It commonly occurs as thin white coatings on smithsonite near the surface. In the zinc deposits of Yellow Pine, Nev.,[6] the outcrops of most of the zinc-lead deposits are marked by soft, white, chalklike hydrozincite and more or less cerusite and a yellow lead mineral, probably pyromorphite.

At Tintic, Utah,[7] it appears as white, chalky patches, specks, and layers in smithsonite. Some of it was probably derived from smithsonite. It is commonly developed in the zinc-lead ores of Joplin, Mo., and neighboring districts.

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[1] Spencer, A. C., U. S. Geol. Survey Geol. Atlas, Franklin Furnace folio (No. 161), 1908.

[2] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 111, 1905.

[3] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 294, 1911.

[4] Spencer, L. J., On hopeite and other zinc phosphates and associated minerals from the Broken Hill mines, northwestern Rhodesia: Mineralog. Mag., vol. 15, p. 3, 1908.

[5] Friedel, C., and Sarisin, E., Sur la composition de la hopeite: Soc. min. France Bull., vol. 2, pp. 153–156, 1879. De Schulten, A., Production artificielle de la hopeite: Soc. min. France Bull., vol. 27, pp. 100–103, 1904.

[6] Hill, J. M., op. cit., p. 244.

[7] Loughlin, G. F., op. cit., p. 3.

Aurichalcite, a basic carbonate of zinc and copper, is deposited by cold descending solutions, generally as drusy incrustations. It is developed sparingly in some of the zinc deposits of the Mississippi Valley. In the Cerro Gordo mine, Cal., according to Knopf,[1] it occurs locally in some abundance as small veinlets traversing zinciferous limonite. Characteristically it forms rosettes and fanlike groups of pearly luster. At Tintic it occurs as drusy incrustations[2] or divergent tufts of crystals, or as minute crystals associated with hydrozincite and smithsonite. In the Magdalena district, New Mexico,[3] aurichalcite occurs in druses and also enveloped in calcite crystals.

Wurtzite, ZnS, the hexagonal form of zinc sulphide, is secondary. In the San Francisco district, Utah, according to B. S. Butler,[4] it is abundant in the Horn Silver mine. It occurs most commonly as growths on sphalerite and as films coating walls of cleavage cracks in sphalerite. The zinc sulphides of the Horn Silver mine are honey-yellow in color. On superficial examination the zinc sulphide ore appears to be composed of one mineral, but in thin sections under the microscope two minerals, one isotropic and another double refracting, are apparent,[5] as shown by Plate IV, *B* (p. 138). Wurtzite is most abundant in the highly brecciated ore, which is the richest in zinc. The fact that wurtzite is practically absent from the massive primary ore supports the conclusion that it is secondary. Wurtzite is found also in the upper levels of the Gagnon mine at Butte, Mont.[6]

Sphalerite, ZnS, is a persistent mineral. Large bodies of sphalerite ore are found in contact-metamorphic deposits and in veins formed at great and at moderate depths. It is also found in deposits formed by cold solutions in regions remote from igneous rocks.

Zinc sulphide crystallizes in two different forms, sphalerite, or zinc blende, which belongs to the isometric system, and as wurtzite, which belongs to the hexagonal system. Sphalerite is the most abundant primary ore of zinc and in most deposits of sulphide ores it is the only important primary zinc mineral.

Though a crystalline precipitate is under some conditions formed from zinc salts in cold waters, the available laboratory experiments show that the precipitate from zinc salts by alkali sulphides in the cold, or at the boiling point, under ordinary conditions gives no indications of crystallinity; but when fairly concentrated solutions of

[1] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 105, 1914.

[2] Loughlin, G. F., op. cit., p. 8.

[3] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 253, 1910.

[4] Butler, B. S., Geology and ore deposits of San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 149, 1913.

[5] Idem, p. 93.

[6] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 80, 1912.

the soluble sulphides act on amorphous zinc sulphide at higher temperatures, sphalerite is precipitated. A solution of 10 per cent potassium sulphide heated with amorphous zinc sulphide at 100° to 200° for two months gave sphalerite and never wurtzite. In acid solutions zinc sulphide was precipitated as wurtzite.[1]

A few observations on the occurrence of secondary sphalerite are noteworthy. At Leadville, Colo., according to Blow,[2] a large proportion of the zinc removed from the carbonate zone by surface waters was probably redeposited as sulphide in the lodes just below the line of complete oxidation. In Shasta County, Cal., according to Graton,[3] sphalerite that is later than pyrite is found in the sulphide zones of copper deposits in association with minerals that are probably in part of secondary origin. At Rio Tinto, according to Finlayson,[4] some sphalerite is later than pyrite and chalcopyrite. At Breckenridge, Colo., according to Ransome,[5] some of the sphalerite is younger than the earliest period of deposition, although it can not be shown that it is a deposit of sulphate waters. Clarke[6] mentions the occurrence of stalactites of sphalerite, a form that suggests secondary deposition. At Galena, Kans.,[7] drifts in a deposit of sphalerite and galena 80 feet below the surface were covered with 3 feet of white mud, consisting mainly of zinc sulphide, with a little iron sulphide, sulphur, and silica. The deposit covered more than 5,000 square feet. The water from the mud is acid, but no hydrogen sulphide was noted.[8] Notwithstanding these well-authenticated examples of secondary deposition of zinc sulphide, there is not much evidence that zinc blende is precipitated by secondary processes along with copper, silver, and gold. The high solubility of its sulphate favors its transportation to points beyond the zones where these metals are precipitated.

ZINC-BEARING DEPOSITS.[9]

WISCONSIN ZINC AND LEAD DEPOSITS.

In the upper Mississippi Valley, in southwestern Wisconsin and northwestern Illinois, in an area extending into Iowa, there are

[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: Am. Jour. Sci., 4th ser., vol. 34, p. 355, 1912.

[2] Blow, A. A., The ore chutes and recent developments of Iron Hill, Leadville, Colo.: Am. Inst. Min. Eng. Trans., vol. 18, p. 172, 1890.

[3] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 100, 1910.

[4] Finlayson, A. M., The pyritic deposits of Huelva, Spain: Econ. Geology, vol. 5, p. 417, 1910.

[5] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 169, 1911.

[6] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 675, 1916.

[7] Iles, M. W., and Hawkins, J. D., The occurrence of amorphous sulphide of zinc near Galena, Mo.: Eng. and Min. Jour., vol. 49, p. 499, 1890.

[8] Robertson, J. D., On a new variety of zinc sulphide from Cherokee County, Kans.: Am. Jour. Sci., 3d ser., vol. 40, p. 161, 1890.

[9] Some deposits containing zinc are described in the sections treating deposits of copper, lead, and silver.

numerous deposits of zinc and lead sulphides.[1] The rocks of this area are sedimentary beds, consisting of limestone, sandstone, and shales. The rocks dip gently to the southwest and in some places there are small shallow structural troughs or synclines. The beds are fissured and heavily jointed but are not displaced by faulting, except locally by faults of very slight throw. There are no igneous rocks exposed in this region.

A section showing the age, character, and thickness of the beds is given below. The ores are principally in the Galena limestone, though some are in the Platteville and a little in the Maquoketa shale above the Galena. Most of the workable deposits are near the base of the Galena, though some are in its upper part and others below the base.

Section in the upper Mississippi Valley.

System.	Group and formation.	Character.	Thickness in feet.
Quaternary.		Alluvium. Terrace deposits. Drift and loess. Residual clays.	0–300
Silurian.	Niagara dolomite.	Dolomite.	150–250
Ordovician.	Maquoketa shale. Galena dolomite. Decorah shale. Platteville limestone. St. Peter sandstone.	Shales. Dolomite. Shale. Limestone and dolomite. Sandstone.	150–250 350 25–100
	Prairie du Chien group. Shakopee dolomite. Oneota dolomite.	Dolomite. Dolomite.	50–100 50–275
Cambrian.		Sandstone with minor shale and dolomite.	800
Pre-Cambrian.		Quartzite, with igneous intrusions.	

A generalized section of the Galena and adjacent formations near the main ore horizon is given below:

	Feet.
Galena dolomite:	
Cherty dolomite	100
Dolomitic limestone, free from chert (maximum)	50
Oil rock (maximum)	6
Decorah shale:	
Shale or blue clay, called the "clay seam" (maximum)	4
Brittle limestone, "glass rock."	
Platteville limestone:	
Magnesian limestone.	

[1] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Wisconsin Geol. Survey, vol. 4, pp. 378–575, 1882. Van Hise, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng. Trans., vol. 30, 1900. Grant, U. S., Lead and zinc deposits of Wisconsin: Wisconsin Geol. Survey Bull. 9, 1903. Bain, H. F., Zinc and lead deposits of the upper Mississippi Valley: U. S. Geol. Survey Bull. 294, 1906. Cox, G. H., Lead and zinc deposits of northwestern Illinois: Illinois State Geol. Survey Bull. 4, 1910. Cox, G. H., The origin of lead and zinc ores of the upper Mississippi Valley district: Econ. Geology, vol. 6, pp. 427–448, 582–603, 1911.

The shale or clay seam is at the top of the Decorah shale. The oil rock is an impure shaly limestone rich in organic matter, which, according to David White,[1] is composed chiefly of microscopic algæ.

The distillation product of the oil rock was analyzed by R. T. Chamberlin, who says that the oil rock is very porous and light, having a specific gravity of only 1.98 and yielding gas bubbles when placed in water. One volume of the rock gave 57.46 volumes of gas when heated to a red heat in a vacuum for two hours. An analysis of this gas gave the following results:

Analysis of gas from oil rock from Dugdale prospect, Wisconsin.

Hydrocarbon vapors	11.11
Heavy hydrocarbons	4.00
CH_4	35.98
H_2S	6.79
CO_2	18.12
CO	8.40
O	.26
H_2	13.18
N_2	2.21
	100.05

The ore deposits are in "crevices," in "runs," are disseminated in beds, and are in "flats and pitches." The crevices, called by J. D. Whitney "gash veins," are fissures and persistent joints enlarged somewhat by solution and cemented with ore. Certain beds appear to be particularly favorable to concentration of the ore, and where these are cut by crevices, flat-lying irregular ribbons of ore, termed "runs," are developed at and near the intersections.

The ores in the flats follow the flat beds, and the ore in the pitches follows crevices, which pitch or dip away about 45° from either side of the vertical crevices. The pitches of a deposit join at the end, making in plan a long, slender ellipse where they intersect the oil rock. The form of the whole body has been compared by Chamberlin to the domestic flatiron. The top and bottom of the iron are flats; the sides are pitches. As shown by U. S. Grant, this is a very common structural type. Commonly the interior of the structure is partly filled with low-grade disseminated ore, so that long and relatively narrow masses are worked. Deposits that are largely workable are commonly as much as 1,000 feet long, 75 feet wide, and 40 or 50 feet high.

The genesis of these deposits, as worked out by Chamberlin, Grant, and Bain, is essentially as follows: The lead, zinc, and iron were deposited on the sea bottom when the Galena dolomite was formed. The metals were probably taken into solution as sulphates and chlorides and were reduced by organic matter to sulphides at the time of their deposition. Later, when the beds were elevated and

[1] Bain, H. F., op. cit., p. 26.

the Maquoketa shale was removed, the ground water circulated more actively through the rocks. According to Cox,[1] the Maquoketa shale also carried original sulphides and was a source of considerable ore. The ground waters at this stage were oxidizing, and the metals were then dissolved, probably as sulphates or as carbonates. The crevices, or enlarged joints, and the flats and pitches opened by stresses and by settling of the limestone above the shrinking oil rock, were filled with ore and the rock near by was replaced metasomatically by the ore-depositing solutions. Hydrogen sulphide from the oil rock precipitated the metals as sulphides. Locally the oil rock was replaced also. The ore itself was somewhat brecciated by further settling, and the fragments of ore were cemented by calcite and other minerals.

It is noteworthy that the "clay seam" at the top of the Decorah shale generally seals off an artesian circulation in sandstone beds below the Platteville limestone.[2] The ores must therefore have been deposited by descending waters. The gentle synclinal troughs which many of the deposits occupy are believed to be the original troughs of the sea bottom subsequently accentuated by gentle compressive stresses. In such troughs the oil rock is thickest,[3] and in them above the clay seam the descending waters converge. The oil rock would have shrunk most where it was thickest, so that fractures would occur notably in thick parts of the oil rock, particularly where thick parts were surrounded by thin parts, so as to permit greater differences in settling.

The mineral composition of the ores is simple. The minerals are sphalerite, galena, marcasite, calcite, and rarely barite. Precious metals and cadmium are not found. Quartz is practically absent. The wall rock is essentially unchanged near the ore deposit, and shows no evidence of hydrothermal action. To a large extent the deposits fill fractures, though some replace the limestone wall rock. As a rule marcasite was formed first and was followed by sphalerite, which was followed by galena. Near the surface sphalerite has been changed to smithsonite and calamine, and much has been removed by solution, leaving a concentration of galena associated with limonite, anglesite, and cerusite. The lead sulphide persists at the very surface, and deposits have been discovered by farmers when they plowed up galena in their fields.

JOPLIN REGION, MISSOURI.

The Joplin region is in southwestern Missouri and neighboring parts of Kansas, Oklahoma, and Arkansas. Although zinc and lead

[1] Cox, G. H., The origin of lead and zinc ores of the upper Mississippi Valley district: Econ. Geology, vol. 6, p. 602, 1911.

[2] Bain, H. F., Flats and pitches of the Wisconsin lead and zinc district, in Types of ore deposits, p. 82, San Francisco, 1911.

[3] Grant, U. S., op. cit.

are found in an area of about 3,100 square miles, more than four-fifths of the zinc ore produced comes from an area of 100 square miles centering about Joplin and Webb City and lying within 14 miles of Joplin. It is the most productive zinc-bearing region in the United States.

All the rocks of the region are sedimentary.[1] They dip southwestward, away from the Ozark uplift, at very low angles. The surface is a rolling prairie. Carboniferous rocks only are exposed. Most of these are Mississippian, but here and there small remnants of Pennsylvanian rocks are found. According to Siebenthal the following formations are represented:

	Thickness in feet.
Cherokee formation (Pennsylvanian):	
Shale, sandstone, and coal beds; top eroded. At some places the formation rests on the Carterville, at others on Boone limestone; at many places the entire formation has been removed by erosion	0–150+
Unconformity.	
Carterville formation (Mississippian):	
Shale and sandstone; rests on eroded surface of Boone; not everywhere present	0–50
Unconformity, marked by an erosion surface of the Boone, with valleys and ridges.	
Boone limestone (Mississippian):	
Thick, cherty limestone. It contains the Grand Falls chert member, from 15 to 120 feet thick. The top of the Boone is an erosion surface subsequently covered by later Mississippian or by Pennsylvanian shale and sandstone. The Boone is the principal ore-bearing formation. The "sheet ground" is in the Grand Falls chert	145–485

The table above includes two erosion unconformities, one below and the other above the Carterville. The importance of these can not be too strongly emphasized. During these two periods the Boone limestone was deeply trenched and a karst topography—that is, one characterized by underground drainage—was developed. Caves were formed, perhaps of the same order of magnitude as the Mammoth Cave of Kentucky, and limestone sinks were numerous. The country was near sea level,[2] and solution greatly exceeded erosion. Great

[1] Bain, H. F., Preliminary report on the lead and zinc deposits of the Ozark region (with C. R. Van Hise and G. I. Adams): U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, pp. 23–228, 1901. Smith, W. S. T., and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), 1907 (reprinted, 1914). Siebenthal, C. E., Structural features of the Joplin district: Econ. Geology, vol. 1, pp. 119–128, 1906; Origin of the zinc and lead ores of the Joplin region, Missouri, Kansas, and Oklahoma: U. S. Geol. Survey Bull. 606, 1915. Buckley, E. R., and Buehler, H. A., The geology of the Granby area: Missouri Bur. Geology and Mines, 2d ser., vol. 4, 1909. Haworth, Erasmus, Relation between the Ozark uplift and ore deposits: Geol. Soc. America Bull., vol. 11, pp. 231–240, 1900; Special report on lead and zinc: Kansas Univ. Geol. Survey, vol. 8, 1904.

[2] Buckley, E. R., in Bain, H. F., and others, Types of ore deposits, p. 118, San Francisco, 1911.

bodies of residual chert accumulated on the surface, particularly on hillsides and along cliffs bordering streams. This residual chert, typically shown in the Granby district, has been called by Buckley and Buehler the Granby formation. The residual chert and the underlying parts of the Boone were covered over by the Carterville. Later the Carterville was eroded in places and the Cherokee was deposited on the eroded surface of the Boone or, where it was present, on the Carterville. After the Boone limestone had been buried below later beds it evidently contained, at or near its top, water channels, such as solution cavities or openings in buried talus or chert. In places, as Siebenthal has shown, the beds above these solution cavities slumped down, resulting in solution faults.[1] The cavities and breccia were later cemented by ores.

The principal minerals are galena, sphalerite, and their alteration products, such as smithsonite and anglesite, as well as some pyrite, marcasite, and chalcopyrite, and their alteration products. The gangue is chert, calcite, dolomite, and jasperoid. Associated with the ore at many places in the sedimentary beds is a hydrocarbon called "tar," which is supposed to be concentrated from organic matter. The chert is abundant. The older residual chert is cemented by a later variety, presumably deposited from the ore-bearing solutions.

The deposits in the "sheet ground" are extensive and lie flat along certain horizons, mainly in the Grand Falls chert member. The ore zones are about 15 feet thick and the ore has been deposited by replacement and by filling openings around chert or in old solution cavities.

The metals were doubtless dissolved by oxidizing waters. The ore-bearing solutions circulated in the breccia and the ancient caves, and the metals were deposited in them in part by reduction through the agency of organic material in the rocks. The source of the solutions is a matter of controversy. Buckley and Buehler think they moved downward from higher rocks, now generally eroded. Bain and Van Hise maintain that they circulated down the southwest slope of the Ozark uplift and rose along faults in the Joplin region. Siebenthal[1] found that some of the faults were formed by downfall or caving of beds above solution cavities, and as they did not extend below the cavities they could not offer deep channels. He attributes the metallization to ascending waters which circulated through cracks and joints, particularly where the shale had been removed by erosion.[2]

[1] Siebenthal, C. E., Structural features of the Joplin district: Econ. Geology, vol. 1, p. 126, 1906.

[2] Siebenthal, C. E., Spring deposits at Sulphur Springs, Ark., with microscopic examination by H. E. Merwin: Econ. Geology, vol. 9, pp. 758–767, 1914; Origin of the zinc and lead deposits of the Joplin region, Missouri, Kansas, and Oklahoma: U. S. Geol. Survey Bull. 606, 1915.

He reports several analyses of muds that settled from artesian waters in this region and that contain zinc and lead and a little copper. Analyses of these waters and their deposits, and also of waters of the vadose circulation, are discussed in this bulletin on pages 103 and 104.

At places where downward-moving waters have altered the ores galena is concentrated near the surface with its oxidation products and with smithsonite, calamine, and limonite. At depths sphalerite and iron sulphide predominate.

LEADVILLE, COLORADO.

The geology and ore deposits of Leadville are discussed in this paper on pages 280–282. The district lies in an area of Paleozoic limestones, quartzites, and shales intruded by dikes and sills of acidic porphyries and extensively faulted after the intrusions. The most valuable deposits are lead-silver ores composed of pyrite, galena, sphalerite, and other minerals, which occur in limestone below the porphyry sheets. The oxidation of sulphide ore in the limestone commonly results in segregations of lead and zinc, and the zinc makes out from the lead here and there on all sides. Zinc deposits occur also in the limestone at or just below its contact with porphyry. Workable deposits of oxidized zinc ores[1] are found in both the "Blue" and the "White" limestone, but principally in the "Blue," which is at a horizon above the "White." The oxidized zinc ore bodies are irregular in outlines and show tendencies to follow bedding planes and contacts. Many of the zinc deposits are near the oxidized iron and lead deposits, but some are far from them and some lie directly below the sulphides. The principal minerals of the oxidized zinc ores are smithsonite, calamine, and hydrozincite. Limonite is a common associate. In general, where iron and zinc have been carried out from the original lead-silver ore bodies the zinc has migrated into the limestone wall rock farther than the iron.

TINTIC, UTAH.

The Tintic district (see pp. 285–289) is a region of folded Paleozoic limestones[2] and other sedimentary rocks overlain by rhyolite and andesite and intruded by monzonite and basalt. The principal ore deposits are great fractured zones and chambered deposits in sedimentary rocks, chiefly limestone, and fissure veins in igneous rocks. The water level in the limestones is deep and some of the oxidized

[1] Butler, G. M., Some recent developments at Leadville: Econ. Geology, vol. 8, p. 1, 1913. Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, p. 282, 1914.

[2] Tower, G. W., jr., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, pp. 603–767, 1899.

ores lie about 2,400 feet below the surface. The primary minerals are pyrite, galena, enargite, chalcopyrite, and tennantite, in a gangue of quartz, barite, and carbonates. Very little zinc sulphide remains. The galena ore, which carries considerable silver, is the most valuable. It is generally partly oxidized, and in several mines in the limestone surrounding the old lead-silver stopes valuable deposits of smithsonite ores[1] have been developed. These ores consist of smithsonite, monheimite, calamine, hydrozincite, and aurichalcite. They are commonly found in the footwalls of the deposits of lead ore or in fractures or along bedding planes. Exceptionally they are found in the hanging walls of stopes. They are associated with iron oxide, which commonly is deposited between the lead ore and the zinc ore. (See p. 376.)

CERRO GORDO MINE, CALIFORNIA.

The Cerro Gordo mine[2] is east of Owens Lake, near the summit of the Inyo Mountains, Cal. The country rock is a dense marble, with which are associated interstratified Carboniferous slate and dikes of diorite and of monzonite porphyry, which lie approximately parallel to the strata. The region was extensively faulted both before and after the deposition of the ores.

The lead ore bodies of the Cerro Gordo mine consist of lenticular masses in the crushed limestone, distributed through a zone 2,000 feet long and several hundred feet wide. The chief primary mineral is galena; minor constituents are sphalerite, tetrahedrite, and pyrite. By oxidation many secondary minerals have formed, including cerusite, bindheimite, smithsonite, calamine, hydrozincite, aurichalcite, chrysocolla, linarite, brochantite, caledonite, and limonite.

In the earlier days of exploitation the principal minerals were argentiferous galena with its alteration products, cerusite and anglesite. The alteration extends to moderate depths. A streak of galena ore on the 700-foot level, according to Knopf,[3] commonly carried cerusite and anglesite, mixed with yellow ocher. The zinc ore forms irregular masses and pipes in the limestone, principally in the footwall, following in general the fractures, joints, and seams of stratification. Near the old lead stopes there are considerable bodies of limonite and nearly pure halloysite; farther away along the secondary deposits zinc carbonate increases and iron carbonate decreases. These bodies extend laterally in places at least 100 feet away from the lead ore.

[1] Loughlin, G. F., The oxidized zinc ores of the Tintic district, Utah: Econ. Geology, vol. 9, p. 1, 1914.

[2] Knopf, Adolph, Mineral resources of the Inyo and White mountains, Cal.: U. S. Geol. Survey Bull. 540, p. 97, 1914.

[3] Idem, p. 104.

MAGDALENA DISTRICT, NEW MEXICO.

The Magdalena district[1] is in Socorro County, N. Mex., at the north end of the Magdalena Range. The district is an area of Carboniferous limestones, which rest on pre-Cambrian crystalline rocks and are in places covered by lavas. Mineralization is due probably to granite porphyry, dikes of which cut the limestone, causing contact metamorphism with development of epidote, pyroxene, and tremolite. The limestone beds are tilted 30° or more and are faulted into blocks. In the Graphic and Kelly mines the chief mineralization is concentrated below gentle arches that pitch westward with the beds, and are mineralized for a maximum distance of 2,000 feet. The structural relations resemble those in the Elkhorn mine, Montana. Five zones of the limestones are mineralized, but only one is a heavy producer. This bed is just below the "Silver Pipe" limestone, and contains large ore bodies, some of them 40 feet thick. The ore deposits, which are replacements of the limestone, contain lead, zinc, iron, copper, gold, and silver. The chief ores of the district are the carbonates and sulphides of lead and zinc. Oxides of copper occur in small quantities in the upper workings. Deeper workings show considerable sulphide of zinc associated with the sulphides of lead and copper. Gold and silver usually occur in small amounts only. Until recent years efforts were confined to the extraction of the lead carbonate ores that lay near the surface. The yellowish or brownish gray zinc carbonate associated with the lead was not recognized but has recently become an important ore.

Many of the ore bodies in the oxidized zone show a concentric arrangement, lead carbonate occurring within and zinc carbonate forming a more or less irregular shell on the outside. Between the two carbonates there is usually a zone of iron oxide or copper oxide, and in places some unoxidized sulphides still remain. The shell of the zinc carbonate is usually much thicker on the under side of the deposit than elsewhere, and in its outer periphery the deposit shows a gradual transition from ore to unaltered limestone.

In the Kelly mine[2] the zinc and the lead ores have been separated by weathering to a notable degree. The oxidized zinc ores form wide stopes, in which there are large caves coated with beautiful light-green smithsonite, in crusts almost 3 inches thick, and beneath the crust is a dark powdery material carrying much manganese and zinc. The lead stopes are much smaller and are composed of almost pure lead carbonate, with some galena.

[1] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 241–258, 1910.

[2] Idem, p. 55.

YELLOW PINE DISTRICT, NEVADA.

The Yellow Pine mining district[1] is in the southwestern part of Clark County, Nev., near the California line. The district is a small but fairly steady producer of zinc, lead, silver, gold, and copper. The country rock is mainly Carboniferous limestone, cut by porphyry dikes and capped by andesite flows. The rocks are folded and extensively faulted. The ore bodies are zinc-lead and copper replacement deposits in limestone and gold deposits in altered igneous rocks. The zinc-lead deposits are the most valuable. The original ore was probably sphalerite and galena, but that now mined is greatly oxidized, the alteration products including smithsonite, cerusite, anglesite, calamine, hydrozincite, and pyromorphite. The lead concentrates carry about 40 ounces of silver to the ton and the zinc concentrates only about 5 ounces.

As a rule lead and zinc are closely associated; in several of the mines the separation is not so clean as in some other regions—for example, at Cerro Gordo, at Tintic, and Magdalena. At some places the ore may be exclusively zinc, yet near by it may be half lead and half zinc, or largely lead. In some of the mines, however, the two kinds of ore, according to Hill, are rather thoroughly separated. At the Bonanza mine there is a deposit of lead ore and an equally clean and distinct deposit of zinc, separated by about 150 feet of limestone. Clean zinc ore, with almost no lead, is found at the Monte Cristo mine and in the stopes of several other mines.

CADMIUM.

PRINCIPAL CADMIUM MINERALS.

The principal cadmium minerals are:

Basic cadmium carbonate	(?)
Cadmium oxide	CdO.
Greenockite	CdS.

SOLUBILITIES OF CADMIUM SALTS.

One thousand grams of a saturated solution[2] at 20° C. contains 433.7 grams of cadmium sulphate, $CdSO_4$, or 573.5 grams of cadmium chloride, $CdCl_2$, or, at 25° C., 0.0026 gram of cadmium hydroxide, $Cd(OH)_2$. The hydrated solid phases of the first two salts are $3CdSO_4.8H_2O$ and $CdCl_2.H_2O$.

NATURE AND RELATIONS OF CADMIUM MINERALS.

Cadmium is bivalent in all of its compounds. It forms a stable oxide, hydroxide, and carbonate. Chemically it resembles zinc and

[1] Hill, J. M., The Yellow Pine mining district, Clark County, Nev.: U. S. Geol. Survey Bull. 540, p. 223, 1914.

[2] Seidell, Atherton, Solubilities of inorganic and organic substances, p. 289, 1912. Higher values are given by Roscoe, H. E., and Schorlemmer, C., Treatise on chemistry, vol. 2, p. 507, 1898.

when found in mineral deposits is almost invariably associated with zinc sulphide ores. The chloride and sulphate are highly soluble, the oxide and carbonate less so. Wells has recently shown that cadmium is more readily precipitated by carbonates than other common metals, except mercury, lead, and copper.[1] Smith states that the normal carbonate, $CdCO_3$, is thrown down, not a basic carbonate.[2] Clarke,[3] however, reports a recent discovery of the basic carbonate, and Leitmeier[4] states that a basic carbonate, otavit, is found in German Southwest Africa. It contains 61.5 per cent CdO. Cadmium sulphide is more soluble in water than copper sulphide. It is dissolved in acid in the absence of an oxidizing agent, when copper sulphide is untouched. Cadmium sulphide, since it is less soluble than zinc sulphide, is precipitated by hydrogen sulphide in solutions acid enough to hold up zinc, and it commonly incrusts cadmium-bearing zinc sulphide that is undergoing alteration. Thus it will be separated from copper in the absence of an oxidizing agent (ferric iron) and from zinc in solutions of low acidity. Cadmium sulphide oxidizes to sulphate, the solid phase of the solution being $3CdSO_4.8H_2O$. I have been unable to find an occurrence of the salt in mineral deposits. It is very soluble in water. A sample of water from the St. Lawrence mine at Butte, Mont., contains 41 parts cadmium per million. (See No. 6 in table on p. 87.)

Cadmium carbonate occurs in the Tschumeb mine, in German Southwest Africa.[5]

Cadmium oxide, CdO, occurs, according to Clarke,[6] in crystallized form. The nature of the occurrences are unknown to me.

Greenockite, CdS, is the principal ore of cadmium. Unlike iron, mercury, and zinc, cadmium forms but one sulphide. Greenockite is probably primary as well as secondary. Amorphous cadmium sulphide may be formed synthetically by precipitation from solutions with hydrogen sulphide, or with alkaline sulphides. By heating the amorphous sulphide with alkaline sulphide in a sealed tube[7] to 150° to 200° greenockite is formed.

When acid solutions of cadmium salts are precipitated by hydrogen sulphide, the product may be either amorphous or crystalline, its form depending on the conditions and the rapidity of precipitation. Large crystals were obtained by heating in a sealed tube

[1] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

[2] Smith, Alexander, General inorganic chemistry, p. 651, New York, 1907.

[3] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 669, 1916.

[4] Doelter, C., Handbuch der Mineralchemie, Band 1, p. 508, 1912.

[5] Schneider, O., Centralbl. Mineralogie, 1906, p. 388; cited by Doelter, C., Handbuch der Mineralchemie, Band 1, p. 508, 1912. The original is not accessible to me.

[6] Clarke, F. W., op. cit., p. 669.

[7] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions; microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 34, p. 341, 1912.

at 180°. As yet the crystalline sulphide has not been produced in the cold by laboratory experiments with either acid or alkaline solutions.

Cadmium is present in zinc sulphide ores in several districts. In the Joplin (Mo.) district zinc ores commonly carry 0.1 to 0.7 per cent cadmium.[1] Whether the sulphide is present in the primary ore as greenockite or isomorphous with zinc sulphide is uncertain. Cadmium is present also in zinc ores of Leadville, Colo. At the Moscow mine, San Francisco region, Utah,[2] greenockite was noted as films on or replacing sphalerite. It has been reported also from the zinc deposits of Hanover district, New Mexico. In the lead, zinc, and fluorspar deposits of western Kentucky[3] greenockite is generally found where sphalerite is being altered, and when sphalerite is abundant greenockite is very common. Cadmium sulphide coats over and fills cracks in both the ore and rocks; much of it is formed near and usually a little above the water level at the expense of zinc sulphide. At Joplin, also, secondary greenockite is found coating crystals of sphalerite.[4]

MERCURY.

PRINCIPAL MERCURY MINERALS.

The principal mercury minerals are:

Native mercury, quicksilver	Hg.
Amalgam	AuHg.
Calomel	HgCl.
Terlinguaite	Hg_2ClO.
Eglestonite	Hg_4Cl_2O.
Montroydite	HgO.
Metacinnabar	HgS.
Cinnabar	HgS.
Schwatzite, mercurial tetrahedrite	$4(Cu_2,Hg_2)S.Sb_2S_3$.
Coloradoite	HgTe.
Tiemannite	HgSe.
Onofrite	Hg(Se.S).

SOLUBILITIES OF SALTS OF MERCURY.

The solubilities of the several salts of mercury in a liter of water are shown in the table on page 393. Unless otherwise noted the number in each square shows the number of grams of the anhydrous salt held in solution in a liter of water (see footnotes).

[1] Waring, W. G., The volumetric determination of zinc: Am. Chem. Soc. Jour., vol. 26, p. 16, 1904.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 93, 1913.

[3] Ulrich, E. O., and Smith, W. S. T., The lead, zinc, and fluorspar deposits of western Kentucky: U. S. Geol. Survey Prof. Paper 36, p. 146, 1905.

[4] Siebenthal, C. E., U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 794, 1909.

Hg_2SO_4.[a]	HgCl.[b]	$HgCl_2$.[c]	$HgBr_2$.[d]	HgBr.	HgI_2.[e]	HgO.[f]	HgS.[g]
0.068	0.002	69.0	6.1	0.000039	0.054	0.0518	0.00012

[a] In solution with 1.96 grams H_2SO_4 at 25°. Drucker, quoted by Seidell, Atherton, Solubilities of inorganic and organic substances, p. 200.

[b] One liter water at 13°. Kohlrausch, Zeitschr. physikal. Chemie, 1904, p. 356.

[c] Mercuric chloride per 1,000 grams solution at 25°. Foote and Levy; Seidell, Atherton, op. cit., p. 190.

[d] Mercuric bromide at 25°. Seidell, Atherton, op. cit., p. 190.

[e] Mercuric iodide, HgI_2, gram per liter at 22°. Rohland; Seidell, Atherton, op. cit., p. 197.

[f] Yellow HgO in 1,000 cubic centimeters solution at 25°. Schiek; Seidell, Atherton, op. cit., p. 200.

[g] Freshly precipitated HgS at 18°. Weigel, O., this paper, p. 117.

NATURE AND RELATIONS OF MERCURY MINERALS.

Mercury enters two series of compounds—the mercurous, in which it is univalent, and the mercuric, in which it is bivalent. The halogen salts of mercurous mercury are insoluble, and mercurous chloride, calomel, is a fairly stable mineral, although it is not a common ore. Mercurous chloride is a little more soluble in water than silver chloride and is oxidized to the soluble mercuric salt. Therefore it is less stable in weathered zones. It is much less soluble than lead chloride. Mercuric chloride is highly soluble and does not give insoluble basic salts with water; mercuric sulphate is easily hydrolyzed and gives basic sulphate, which is reduced to native metal. The oxychlorides of mercury, terlinguaite and eglestonite, are rare minerals, known only in the Terlingua district, Brewster County, Tex. The oxide, montroydite, is also restricted, so far as known, to this district. Wells[1] showed that a soluble carbonate will precipitate mercury more readily even than silver and lead. The nature of the precipitate is not known to me. No mercury carbonate is found in mineral deposits.

The following experiments in the solution and precipitation of mercury were made by Mr. T. M. Broderick.[2] Cinnabar was left in contact with one-twentieth normal sulphuric acid, with one-twentieth normal hydrochloric acid, and with one-twentieth normal sulphuric acid and one-twentieth normal ferric sulphate. After 6 weeks 5 cubic centimeters of solution was tested by passing hydrogen sulphide through it. The only experiment which showed a precipitate of mercury sulphide was that made with the solution of hydrochloric acid.

Testing with concentrated solutions showed the same results. A solution of ferric sulphate in strong sulphuric acid was boiled in

[1] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

[2] Broderick, T. M., work in preparation.

contact with cinnabar for 6 hours, and the liquid was then tested for the presence of mercury, but none was found. Cinnabar was treated with hydrochloric acid in the presence of manganese oxide. Much of the cinnabar was dissolved by the nascent chlorine evolved. These results are not surprising, for sulphates of mercury are not very soluble, whereas mercuric chloride is highly soluble, very little ionized, and does not give insoluble basic salts with water. If mercury sulphate forms in mine waters, the process must be very slow compared to solution with chloride. That cinnabar is slowly attacked by some natural alkaline solutions has been shown experimentally by Grout.[1]

Native mercury, which is a fairly common mineral, is doubtless formed when mercury salts are reduced. Organic matter, which is commonly present in cinnabar deposits, may have played a part in reduction, which, however, may be accomplished also in other ways. Native mercury is commonly associated with calcite in cinnabar deposits, and the calcite has possibly played a part in the precipitation of the metal, as is suggested by the following experiment. A saturated solution of mercurous sulphate—that is, about 0.058 grams per liter—was added to a very dilute solution of ferrous sulphate with a little sulphuric acid, and to the mixture calcium carbonate was added. The mixture was warmed. Within a week tiny globules of quicksilver had separated and, with a lens, could be found interspersed among the small crystals of gypsum that had formed by action of the acid on lime carbonate. Possibly this process goes on in nature, but the sulphate, as shown above, forms very slowly, if at all. Mercury chloride is very easily reduced. Even in the air in a few years the solid mercurous chloride may develop microscopic globules of native mercury. In arid regions, where the waters carry chloride, some mercury will be dissolved in hydrochloric acid that forms in presence of sulphuric acid and salt. Where calcite or other neutralizing minerals are present the acidity is reduced and mercury is precipitated.

It is apparent from the table of solubilities, however, that the mercury salts, except mercuric chloride, are only moderately soluble, and chlorides are generally only sparingly present in most mineral waters. Secondary concentrations of mercury are less important than those of copper, silver, and some other metals.

That the oxidation of cinnabar is slow is shown also by its common occurrence in placers. On Elk Creek, Oreg.,[2] cinnabar is found in placers intergrown with normal vein quartz in rounded masses

[1] Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 417, 1913.

[2] Lindgren, Waldemar, The gold belt of the Blue Mountains of Oregon: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 708, 1901.

as large as 3 or 4 inches in diameter. It is found also with black sands in placers on Gold Creek, near Philipsburg, Mont.,[1] at the Manzanita mine,[2] Nevada City, Cal., and in placers of many other districts.

Evidence that mercury sulphide is formed under some conditions by secondary processes is found in certain deposits that contain primary mercurial tetrahedrite (schwatzite). This mineral is found with cinnabar in the Columbia mine, Sumpter district, Oregon.[3] Lindgren states that cinnabar is formed during the oxidation of mercurial tetrahedrite, probably by the action of mercuric sulphate on pyrite.[4] Bancroft suggests that schwatzite is the primary ore from which mercurial ores at Cinnabar, near Quartzite, Nev., have formed.[5]

Mercury sulphide, HgS, is less soluble in water than any of the other sulphides and would be expected to replace them in depth, but I do not know of any examples of pseudomorphs of mercury sulphide after the more soluble sulphides. There are two sulphides of mercury—cinnabar, the red rhombohedral sulphide, and metacinnabar, black and probably isometric. Cinnabar[6] is readily formed by the action of the soluble alkali sulphides on the amorphous black sulphide of mercury. If the black sulphide is heated at 100° with concentrated alkaline sulphide, the product changes in 24 hours to red sulphide. Cinnabar only, and never metacinnabar, according to Allen and Crenshaw, is obtained from alkaline solutions. Both sulphides, however, may be obtained from acid solutions of mercury salts.

The black sulphide may be formed by bringing sulphur and quicksilver into intimate contact by rubbing. Sulphur forms by the action of ferric sulphate on hydrogen sulphide and by other oxidation processes, and at depths where these compounds are generated any native mercury present would tend to change to metacinnabar. Hydrogen sulphide itself would precipitate the black mercury sulphide, and at Idria, above the older cinnabar, metacinnabar is found in hemispherical crystal aggregates, suggesting mercury globules changed to sulphide.[7]

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[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 154, 1913.

[2] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley districts, California: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 119, 1896.

[3] Lindgren, Waldemar, The gold belt of the Blue Mountains of Oregon: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 664, 1901.

[4] Lindgren, Waldemar, Mineral deposits, p. 801, 1913.

[5] Bancroft, Howland, Reconnaissance of the ore deposits in northern Yuma County, Ariz.: U. S. Geol. Survey Bull. 451, p. 84, 1911.

[6] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: Am. Jour. Sci., 4th ser., p. 341, 1912.

[7] Schrauf, A., Ueber Metacinnabarit von Idria und dessen Paragenesis: K.-k. geol. Reichsanstalt Jahrb., Band 41, pp. 379–399, 1891. Neues Jahrb., 1893, Band 1, p. 465. See Allen, E. T., and Crenshaw, J. L., op. cit.; the original is not accessible to me.

At Mercur, Utah, pellets of cinnabar are coated with a black mineral not determined.[1]

Experiments were made by Mr. T. M. Broderick to determine the precipitating action of sulphides on a solution of mercurous sulphate. Saturated solutions of mercurous sulphate were left in contact with pyrite, chalcopyrite, and marcasite that had passed through 40-mesh sieves. Saturated solutions of mercurous sulphate, acidified, were left in contact with the same minerals. Similarly, saturated solutions of mercurous sulphate, acidified with sulphuric acid, and containing ferrous sulphate, were left in contact with these minerals. After two months none of the minerals showed tarnish except those which had been in contact with solutions containing ferrous sulphate, which assumed a brownish color, due to a deposit of ferric hydroxide. Similar tests were made with solutions of mercuric chloride. Fragments of pyrite, chalcopyrite, and marcasite were put in test tubes with a concentrated solution of mercuric chloride. Chalcopyrite was rapidly tarnished. After standing two weeks in contact with the concentrated solutions, marcasite became tarnished, but pyrite did not appear to be affected. Pyrrhotite and stibnite precipitated mercury from mercuric chloride and from solutions of mercuric chloride with acid.

Calomel, HgCl, horn quicksilver, is a sectile, white or dull gray mineral, formed by superficial processes at or near the surface of cinnabar deposits. It is found in fine crystals one-fourth to one-half inch in diameter at Terlingua, Tex.,[2] where it is associated with native mercury and other minerals. It has been recognized at Idria, Austria, and at Mount Avala, near Belgrade, Serbia. It is inconspicuous, so that small bodies might easily be overlooked.

Amalgam, AuHg, is rare as a natural mineral. It is reported, however, from Mariposa, Cal., and from a platinum deposit in Colombia. It is found in placers near Bluff, Seward Peninsula, Alaska.[3]

Terlinguaite, *eglestonite*, *montroydite*, the oxychlorides and oxides of mercury, are found only in a mine in Brewster County, Tex., and are all secondary.[4]

Quicksilver.—Native mercury, quicksilver, is almost invariably a product of surface decomposition, though some have regarded it as primary, because it has been found in deposits at moderately great depths. On the Pacific coast, according to J. Allen Veatch,[5] it occurs in perhaps one-fifth of the deposits, and in some deposits is found at

[1] Spurr, J. E., Economic geology of the Mercur mining district, Utah: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 429, 1895.

[2] Hillebrand, W. F., and Schaller, W. T., The mercury minerals from Terlingua, Tex.: U. S. Geol. Survey Bull. 405, p. 159, 1909.

[3] Hess, F. L., written communication.

[4] Hill, B. F., The occurrence of Texas mercury minerals: Am. Jour. Sci., 4th ser., vol. 16, p. 251, 1903.

[5] Veatch, J. A., The genesis of the mercury deposits of the Pacific coast: Am. Inst. Min. Eng. Bull. 86, p. 218, February, 1914.

considerable depths. Some of these deep occurrences, at least, may be attributed to the free downward movement of the liquid metal, which possesses great mobility. At Cable Mountain, Montana, in the gravels from the Cable placer mine, small globules of rusty quicksilver are found at depths of nearly 100 feet. I have seen as much as a gram obtained from a pan of gravel, clay, and sand. It had obviously worked down nearly to the bottom of the gravel bed since the sluicing of the placer deposits was begun, some 30 years before. At the Neglected mine, near Durango, Colo.,[1] gold ore, partly altered, carries numerous globules of mercury. If both metals had been deposited simultaneously in the native state they would probably have formed amalgam. Native mercury with cinnabar is found in the Red Boy mine, Granite district, Oregon.[2] McCaskey mentions native quicksilver that was deposited from waters piped from hot springs to a bathhouse.[3]

Metacinnabar is regarded as a characteristic secondary mineral. It was found near the surface in the Knoxville district, California, but not at greater depth. A large part of the ores in the Baker mine and in the upper levels of the Reed and the Redington mines, between Knoxville and Lower Lake, Cal., were metacinnabar.[4] In the New Almaden mines, Santa Clara County, Cal., where cinnabar and quartz are intergrown, metacinnabar is crystallized on the quartz and is subsequent to it.[5] At Idria, according to Schrauf, pellets of metacinnabar are found in the upper levels. There metacinnabar is younger than the cinnabar, which underlies it, and some has apparently been formed since the opening of the mines. At Kamloops Lake, British Columbia, metacinnabarite occurs in a dolomite vein that traverses the middle of a rhyolite dike in a basic rock, the dolomite being deposited on the walls and metacinnabar with dolomite toward the middle of the latest fissures.[6] Metacinnabar is found also in a similar vein 10 miles east of Round Mountain, Nev.

Cinnabar is the principal ore of mercury and supplies practically all the metal.[7] It is primary in nearly all its occurrences. As shown by Allen and Crenshaw, it may be deposited by either acid or alkaline solutions, and doubtless some is secondary. Cinnabar is unknown as a mineral of igneous rocks or as a constituent of pegmatites, or of

[1] Emmons, W. H., The Neglected mine and near-by properties: U. S. Geol. Survey Bull. 260, p. 121, 1904.

[2] Lindgren, Waldemar, op. cit., p. 683.

[3] McCaskey, H. D., Quicksilver: U. S. Geol. Survey Mineral Resources, 1911, pt. 1, p. 895, 1912.

[4] Becker, G. F., Geology of the quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, pp. 284, 368, 1888.

[5] Melville, W. H., Metacinnabarite from New Almaden, Cal.: Am. Jour. Sci., 3d ser., vol. 40, p. 293, 1890.

[6] Veatch, J. A., The genesis of the mercury deposits of the Pacific coast: Am. Inst. Min. Eng. Bull. 86, p. 221, February, 1914.

[7] McCaskey, H. D., Quicksilver: U. S. Geol. Survey Mineral Resources, 1911, pt. 1, pp. 889–921, 1912. Becker, G. F., op. cit.

contact-metamorphic deposits. It is formed, however, in veins and similar deposits at all depths, but is most abundantly developed in deposits that were formed relatively near the surface. Although many of its deposits become poor or play out in depth, this fact, as stated by McCaskey, may be due to causes other than surface concentration by superficial alteration. Marcasite, pyrite, antimony and arsenic sulphides, chalcedony, quartz, calcite, and sulphur are common associates of cinnabar. Nearly all its deposits are in areas of late volcanic activity. The close association of the mineral with igneous rocks suggests that igneous agencies and hot waters played a part in its deposition. Indeed, at Steamboat Springs, Nev., and Sulphur Bank, Cal.,[1] cinnabar is now being deposited from hot alkaline waters. Many other cinnabar deposits are near extinct or flowing hot springs.

Some mercury sulphide is secondary, for, as already stated, mercury minerals are dissolved slowly as chlorides and possibly as sulphates, and from the descending solutions mercury sulphide is doubtless precipitated. That cinnabar may be secondary as well as primary is indicated by the syntheses of Allen and Crenshaw, noted above. Cinnabar probably forms as an alteration product of mercurial tetrahedrite. At the Redington mine, California, according to Becker,[2] cinnabar coats over metacinnabar, which suggests that the red is the more stable sulphide. Melville and Lindgren[3] mention small nodules of metacinnabar in ores of Knoxville, Cal. That some cinnabar has formed by secondary alteration in the New Idria mine, Fresno County, Cal., is beyond dispute. In a tunnel that had not been used for years Epsom salts and other secondary minerals had accumulated to depths of 2 inches. In this coating Becker[4] found a small seam of cinnabar that clearly had formed since the mine was opened.

Coloradoite, HgTe; *tiemannite*, HgSe; and *onofrite*, HgSeS, are all rare minerals and all are probably primary.

TIN.[5]

The principal tin minerals are cassiterite, SnO_2, and stannite, Cu_2FeSnS_4. At 19° C. 1 liter of water dissolves 188 grams stannous sulphate, $SnSO_4$. At 15° C. 1 liter of water dissolves 2,698 grams stannous chloride, $SnCl_2$.

[1] Le Conte, Joseph, and Rising, W. B., The phenomenon of metalliferous vein formation now in progress at Sulphur Bank, Cal.: Am. Jour. Sci., 3d ser., vol. 24, p. 23, 1882.

[2] Becker, G. F., op. cit., p. 285.

[3] Melville, W. L., and Lindgren, Waldemar, Contributions to the mineralogy of the Pacific slope: U. S. Geol. Survey Bull. 61, p. 22, 1890.

[4] Becker, G. F., op. cit., p. 307.

[5] Mr. F. L. Hess has read the sections of this bulletin treating tin, tungsten, uranium, and vanadium, and has generously contributed to the discussion valuable data and many references.

Tin is one of the more inert metals, and its great commercial value is due largely to its inertness. As shown above, however, both stannous sulphate and stannous chloride are soluble in aqueous solution; the hydroxide is soluble in dilute sodium hydroxide. Stannous chloride and sulphate are both only partly hydrolyzed in water, though stannic chloride and stannic sulphate are more readily hydrolyzed. An oxidizing solution converts the stannous to the stannic salt; consequently neither chloride nor sulphate of stannous or stannic tin is stable in oxygenated solutions like the mineral waters of upper zones in sulphide ores. Collins states that sulphuric acid dissolves cassiterite very readily if a little metallic zinc is present. Doubtless the zinc or hydrogen formed by zinc and acid permits the tin to remain as stannous salt, which, as stated, is less hydrolyzed. According to Doelter,[1] tin oxide itself is slightly soluble in water. He states that at 80° C. in 22 days 0.7084 gram of tin oxide lost 0.0236 gram. The validity of Doelter's conclusions is in doubt, however, for J. P. Goldsberry recently found that no trace of tin oxide is dissolved in distilled water after several hours' boiling. The method of determination would have detected one part in a million. A number of experiments to ascertain the solubility of tin minerals in acid solution were made also by Mr. Goldsberry, who has kindly supplied some data in advance of publication. Cassiterite and stannite were ground to pass 100-mesh sieves, and 1-gram samples were covered with 25 cubic centimeters of the solutions indicated. Tests made at the end of a month at room temperatures showed that tin was dissolved in certain solutions as indicated below, the results being determined by titration with a solution of ammonium molybdate:

	Tin dissolved.
Cassiterite+HCl (conc.)	Trace.
Cassiterite+N/10 H_2SO_4	Faint trace.
Stannite+N/10 H_2SO_4	Faint trace.
Stannite+N/10 HCl	Faint trace.

As shown by these experiments, the action of acid waters on both cassiterite and stannite is very slight. Tin tends to remain in the upper parts of its deposits, and to accumulate in placers. F. L. Hess, who is familiar with tin ores in widely separated districts of the world, informs me that cassiterite is rarely much corroded. In some of the Cornish tin-copper (cassiterite-chalcopyrite) veins the copper and iron sulphides are leached out from the upper parts of the veins and tin only remains, showing that in sulphate solutions tin oxide is more stable than copper sulphides.

[1] Doelter, C., Einige Versuche über der Löslichkeit der Mineralien: Min. pet. Mitt., vol. 11, p. 325, 1890.

Hydrogen sulphide will precipitate stannous sulphide from an acid solution. There is, however, no simple stannous sulphide in nature. From stannic salts stannic sulphide is first precipitated, but it is not stable in the presence of alkali sulphides, such as sodium sulphide, Na_2S, with which it yields a sulpho-stannate.

$$SnS_2+Na_2S=Na_2SnS_3.$$

With stannous sulphide and sulphur the reaction is

$$SnS+Na_2S+S=Na_2SnS_3.$$

The alkali sulphostannate is unstable in acid solutions. If ferrous iron replaces sodium and a molecule of chalcocite is added the formula becomes that of stannite. The chemical similarity of stannite, the copper-iron sulphostannate, to sulphoarsenates and sulphoantimonates, which are commonly regarded as secondary, suggests that the precipitation of secondary stannite is possible, but few examples of secondary stannite are recorded. Hintze[1] mentions a pseudomorph of stannite after arsenopyrite. The tin boron minerals, nordenskiöldine, hulsite, and paigeite, are all primary.

As already stated, tin shows but little evidence of transportation in most of its deposits. Even when associated with sulphides, cassiterite appears to be stable. Like lead and antimony, it shows strong tendencies to remain in the oxidizing zone. When other metals are present they may be concentrated by superficial alteration, as they would be in the absence of tin ores. Thus in the Cornwall region[2] primary lodes that are assumed to have consisted of tin oxides and copper sulphides have been leached of copper near the surface, while tin remained in upper parts of the lodes. In depth the ores are enriched by secondary deposition of copper. As stated by McAlister,[3] some of these deposits of copper are exceedingly rich; by decrease of copper, tin becomes relatively more abundant at depths, as it is at the surface.

At Potosi, Bolivia, where sulphide ores of silver carry stannite and cassiterite, the silver is greatly concentrated near the surface. Possibly there has been also some secondary concentration of tin. This district, which, according to Wendt,[4] yielded over a billion ounces of silver, is perhaps the most productive silver-producing camp in the world. The deposits are lodes and fractured zones in an intrusive that consists of "rhyolite" (quartz porphyry) and re-

[1] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 1189.

[2] McAlister, D. A., Geological aspects of the lodes of Cornwall: Econ. Geology, vol. 3, pp. 363–380, 1908. Hill, J. B., and McAlister, D. A., Geology of Falmouth and Cornwall, Min. Survey England and Wales, 1906.

[3] McAlister, D. A., op. cit., p. 377.

[4] Wendt, A. F., The Potosi, Bolivia, silver district: Am. Inst. Min. Eng. Trans., vol. 19, p. 70, 1891.

lated rocks. The deeper ore carries considerable pyrite and chalcopyrite, with arsenic and antimony and tin minerals. The ore has been leached of iron by surface decomposition, and iron oxides in the solutions escaping from the deposit have cemented conglomerates on the surface. Evidently the outcropping ore was very rich in silver, for it is said to have been discovered by an Indian who built a fire above the ore and noted streamlets of silver in the ash. Enormous bodies of altered ores ("pacos") were worked, their valuable content being mainly in horn silver and native silver. The deeper lying, partly altered ore ("mulattos") carries more iron oxide, and below this the sulphide ore ("negrillos") is encountered. It carries cassiterite, chalcopyrite, pyrite, and stannite, a little sphalerite and galena, ruby silver, and rich tetrahedrite. With increase of depth more of the veinstuff becomes unworkable, yet the ore has been worked 2,000 feet below the surface.

Tin and silver appear to have been segregated in the upper parts of the lodes, for Wendt states that the earlier miners of silver left tin deposits that were subsequently removed. Much of the tin ore was wood tin, and like silver, it appears to have been concentrated in the oxidized zone.[1] The extent to which tin has been dissolved and reprecipitated by surface agencies is uncertain. Rumbold has described many neighboring tin deposits of the usual cassiterite type, which contain little stannite and appear to be but slightly altered by secondary processes.[2]

Cassiterite, SnO_2, is the principal ore of tin. It is found sparingly in some igneous rocks and is a constituent of some pegmatites[3] and a few contact-metamorphic deposits. It is an important constituent of many tin-bearing veins, nearly all of which are of deep-seated origin and include minerals containing fluorine, boron, or lithium. In veins formed at moderate or shallow depths cassiterite is exceedingly rare, although not unknown. Tin oxide is one of the most stable minerals in ground water,[4] and it accumulates in placers that form the most valuable sources of tin.[5] Some is dissolved, however, and reprecipitated mainly as "wood tin," a botryoidal or reniform variety, which is formed at the surface by processes of decomposition.

According to Collins,[6] masses of wood tin weighing about a pound were found in the Wheal Providence lode, Cornwall. Concretions

[1] Singewald, J. T., Some genetic relations of tin: Econ. Geology, vol. 7, p. 3, 1912.

[2] Rumbold, W. R., The origin of Bolivian tin deposits: Econ. Geology, vol. 4, p. 321, 1909.

[3] Graton, L. C., The Carolina tin belt: U. S. Geol. Survey Bull. 260, p. 188, 1905. Ferguson, H. G., and Bateman, A. M., Geologic features of tin deposits: Econ. Geology, vol. 7, p. 209, 1912.

[4] Hess, F. L., and Graton, L. C., The occurrence and distribution of tin: U. S. Geol. Survey Bull. 260, p. 161, 1905.

[5] Penrose, R. A. F., jr., The tin deposits of the Malay Peninsula: Jour. Geology, vol. 11, p. 135, 1903.

[6] Collins, J. H., On some Cornish tinstones and tin-capels: Mineralog. Mag., vol. 4, p. 1, 1880.

1 to 4 inches in diameter were found in the Prideaux Wood mine. The occurrence of the wood tin on the summits of quartz crystals suggests that the tin has been transferred to some extent during oxidation. Microscopic examination of an incrustation of wood tin on an ingot of tin that had long been buried showed radiate structure and botryoidal form.[1] Great bodies of wood tin occurred with secondary silver at Potosi, Bolivia.[2]

Stannite, tin pyrites, $Cu_2S.FeS.SnS_2$, is found in many tin deposits in Bolivia, particularly at Potosi.[3] According to Rumbold,[4] however, cassiterite is more abundant in some of them. It is known in some of the Cornwall mines, also at Zinnwald, Erzgebirge, and at Wicklow, Ireland. At Lost River, Alaska, stannite is associated in small quantity with galena and wolframite in a gangue of topaz and fluorite.[5] It has been mined from the Conrad and King Conrad mines, Howell, New South Wales,[6] and occurs in notable quantity in the Oonah and Silver Queen mines, at Zeehan and at Heemskirk.[7] At Zeehan it was associated with galena, chalcopyrite, and pyrite, and at the Silver Queen mine it carried about 90 ounces of silver and 0.15 ounces of gold per ton.[8] In Queensland it has been found in several mines in the Walsh and Tineroo mineral fields,[9] and on Stewart's tin claim, near Watsonville, it is associated with cassiterite, chalcopyrite, arsenopyrite, pyrite, wolframite, chlorite, and hydrous iron oxide.[10] These occurrences are not generally regarded as secondary. Hintze,[11] quoting Wedding, mentions pseudomorphs of stannite after arsenopyrite. No occurrences of economic value that are certainly secondary are known to me.

ARSENIC.

PRINCIPAL MINERALS OF ARSENIC.

The names and chemical compositions of the principal arsenic minerals are given on the opposite page.

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[1] Collins, J. H., op. cit., p. 110.

[2] Singewald, J. T., Some genetic relations of tin deposits: Econ. Geology, vol. 7, p. 263, 1912.

[3] Wendt, A. F., op. cit., p. 90.

[4] Rumbold, W. R., The origin of the Bolivia tin deposits: Econ. Geology, vol. 4, p. 321, 1909.

[5] Knopf, Adolph, Geology of the Seward Peninsula tin deposits, Alaska: U. S. Geol. Survey Bull. 358, p. 18, 1908.

[6] Andrews, E. C., The geology of the New England plateau, with special reference to the granites of northern New England: New South Wales Geol. Survey Rec., vol. 8, pt. 3, p. 146, 1905.

[7] Hartwell, Conder, The occurrence of stannite in Australia: Australian Min. Standard, vol. 40, p. 577, 1908.

[8] Petterd, W. F., Catalogue of the minerals of Tasmania, Tasmania Dept. Mines, p. 167, Hobart, 1910.

[9] Dunstan, B., Queensland mineral index and guide: Queensland Geol. Survey Pub. 241, p. 911, Brisbane, 1913.

[10] Jack, R. L., Report on the tin mines of Herberton, Western, and Thompsons Creek districts: Queensland Geol. Survey Pub. 13, p. 26, 1883.

[11] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 1189, 1904.

Native arsenic	As.
Arsenolite	As_2O_3.
Scorodite	$FeAsO_4.2H_2O$.
Annabergite	$Ni_3As_2O_8.8H_2O$.
Erythrite	$Co_3As_2O_8.8H_2O$.
Mimetite	$(PbCl)Pb_4As_3O_{12}$.
Realgar	AsS.
Orpiment	As_2S_3.
Gersdorffite	NiAsS.
Cobaltite	CoAsS.
Chloanthite	$NiAs_3$.
Smaltite	$CoAs_3$.
Tennantite	$4Cu_2S.As_2S_3$.
Proustite	Ag_3AsS_3.
Pearceite	Ag_9AsS_6.
Enargite	Cu_3AsS_4.
Arsenopyrite	FeAsS.
Löllingite	$FeAs_2$.

OCCURRENCES AND RELATIONS OF ARSENIC MINERALS.

Arsenic, antimony, and bismuth are closely related chemically and form corresponding mineral compounds. Arsenic is in the main, however, an acid-forming element and plays the part of a non-metal in its compounds. Antimony is both acid forming and base forming but generally acts as a metal. Native metallic arsenic, arsenolite, and the iron, cobalt, and nickel arsenates, scorodite, annabergite, and erythrite are secondary. The sulphides, realgar and orpiment, are secondary in some occurrences, as are the copper-arsenic sulphide, tennantite; the nickel-arsenic sulphide, gersdorffite; and the silver-bearing arsenic sulphosalts prousite and pearceite. Arsenopyrite and löllingite are always primary, and there are no well-authenticated examples of secondary chloanthite, smaltite, or cobaltite.

The native metal arsenic is not uncommon, as would be expected from its position in the electromotive series, in which it stands between copper and bismuth. Arsenic compounds may form in the presence of oxygen, as arsenolite, As_2O_3. A liter of water at 15° C. dissolves 16.57 grams of arsenolite.[1] If arsenic is present as a salt of H_3AsO_3, much water will hydrolyze it; if present as salt of arsenic, as a base-forming element, these also are hydrolyzed. With water the pentoxide in the presence of an oxidizing agent forms arsenic acid,

$$As_2O_5+3H_2O=2H_3AsO_4.$$

With nickel, Ni″, and cobalt, Co″, arsenic acid, H_3AsO_4, or $H_6As_2O_8$, forms annabergite, $Ni_3As_2O_8.8H_2O$, and erythrite, $Co_3As_2O_8.8H_2O$.

[1] Seidell, Atherton, Solubilities of inorganic and organic substances, p. 42, 1912.

Scorodite, $FeAsO_4.2H_2O$, to compare with annabergite and erythrite, may be written $Fe_2As_2O_8.4H_2O$. Arsenic acid behaves much like phosphoric acid; the compounds pyromorphite, the lead chlorphosphate, and mimetite, the lead chlorarsenate, are closely similar in form and manner of occurrence. See also vanadinite (p. 418).

The arsenates of iron, nickel, and cobalt are fairly stable, especially annabergite and erythrite, which commonly appear in the gossan (cobalt and nickel "blooms"); scorodite, the iron arsenate, can be less easily recognized, a fact due to its comparatively inconspicuous color. Sulphides of both arsenic and antimony are precipitated from acid solutions by hydrogen sulphide, and, like chalcocite, could form in secondary sulphide zones. Moreover, in accordance with their positions in the Schuermann series, they should be expected to replace sulphides of iron and zinc and of some other less common metals, but the evidence of such replacements is meager. Croasdale[1] states, however, that pyrite removed all the arsenic from a solution that had stood 48 hours. In its secondary activities, arsenic, which, as noted above, generally acts as an acid-forming compound, is reprecipitated in sulphosalts of the metals. Among these proustite, pearceite, and tennantite are not uncommon, although they are much less common than corresponding salts of antimony. Although examples of secondary realgar and orpiment are not unknown, I can find no well-authenticated examples of secondary stibnite. As shown by Cooke, stibnite is attacked by argentiferous sulphuric acid solutions depositing mixtures of antimony sulphide and silver sulphide, but no double sulphide was shown to be present.

Alkali sulphides react with sulphides of arsenic, giving soluble complex sulphides.

$$3Na_2S+As_2S_3=2Na_3AsS_3.$$

With such a salt, which is soluble, silver sulphate could form secondary sulphosilver salts.

$$3Ag_2SO_4+2Na_3AsS_3=Ag_6As_2S_6+3Na_2SO_4.$$

If $Ag_6As_2S_6$ is written $3Ag_2S.As_2S_3$, it corresponds to the formula of proustite. The reaction goes on readily also with antimony sulphide,[2] as indicated below:

$$3Na_2S+Sb_2S_3=2Na_3SbS_3.$$
$$3Ag_2SO_4+2Na_3SbS_3=Ag_6Sb_2S_6+3Na_2SO_4.$$
$$Ag_6Sb_2S_6=2Ag_3SbS_3=\text{pyrargyrite}.$$

[1] Croasdale, Stuart, The action of iron sulphides on copper solutions: Eng. and Min. Jour., vol. 97, p. 746, 1914.

[2] Grout, F. F., On the behavior of cold and acid sulphate solutions of copper, silver, and gold, with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 426, 1913.

Native arsenic is formed probably altogether by reduction in the superficial zone. It is said to occur in Nevada in considerable quantity a few miles south of Pyramid Lake,[1] and is reported from Goat Lake, a few miles northeast of Monte Cristo, Wash.[2] It is reported also from a locality near Leadville, Colo., and at Haverhill, N. H., and many European occurrences are known. Commonly it forms nodular masses having concentric shells.

Arsenolite, As_2O_3, is almost unknown, although the corresponding antimony oxides are fairly common. This is due to the greater solubility of the arsenic oxide in water and to its property of hydrolysis in either acid or alkaline solutions as noted above.

Scorodite, $FeAsO_4.2H_2O$, arsenic bloom, is a common oxidation product of arsenopyrite, and, like annabergite and erythrite, is frequently found in the oxidized zone, in which it may persist at the surface. It is unknown in unaltered sulphide ores. It is generally formed at or near the surface but is not always an alteration product. Hague[3] has observed it forming now as an incrustation of springs and geysers in the Yellowstone Park. Small crystals of scorodite are found in the enargite copper ores at Tintic, Utah,[4] and it is an alteration product of arsenopyrite at Monte Cristo, Wash.[5] Scorodite is found as a secondary product, probably after realgar and pyrite, at Mercur, Utah.[6] Although it remains in the oxidized zone, it shows also some mobility, for it is carried down into the rock below the gold-bearing horizon, where other arsenic minerals are said to be absent. Hague[7] states that scorodite deposited in the Yellowstone will itself alter finally to limonite.

Scorodite occurs in a large mass in the outcrop of the ore body of the Gold Hill mine, Gold Hill district, Deep Creek Mountains, Utah.[8]

Annabergite, $Ni_3As_2O_8.8H_2O$ (p. 464), and *erythrite*, $Co_3As_2O_8.8H_2O$ (p. 470), are generically similar to scorodite.

Mimetite, $(PbCl)Pb_4As_3O_{12}$ (chlorarsenate of lead), is an alteration product formed exclusively in oxidized zones. It resembles pyromorphite in form and origin. It is associated with limonite in

[1] Sanford, Samuel, and Stone, R. W., Useful minerals of the United States: U. S. Geol. Survey Bull. 585, p. 116, 1914.

[2] Spurr, J. E., Geology and ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 803, 1901.

[3] Hague, Arnold, Notes on the deposition of scorodite from the arsenical waters of the Yellowstone National Park: Am. Jour. Sci., 3d ser., vol. 34, p. 171, 1887.

[4] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 702, 1899.

[5] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 803, 1901.

[6] Spurr, J. E., Economic geology of the Mercur mining district, Utah: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 392, 1895.

[7] Hague, Arnold, op. cit., p. 172.

[8] Butler, B. S., oral communication.

the Monarch district,[1] Chaffee County, Colo. Mimetite is reported also from the Cerro Gordo mine, Cal. At Eureka, Nev.,[2] mimetite has been found as stalactites, stalagmites, and columns in vugs in some of the ore bodies. Discussing these deposits, Curtis says:

> The arsenopyrite, pyrite, and galena, which formed the original ore, were oxidized, sulphate of iron being first formed. This sulphate of iron trickled down, forming numerous columns, upon which the later product of decomposition, mimetite, was afterward deposited. In time the sulphate of iron lost its sulphuric acid and became limonite, which remained as a core.

Realgar, AsS, is both primary and secondary in its deposits. Like cinnabar it is rare as a primary constituent of deposits formed at great depths. Near Philipsburg, Mont.,[3] realgar is widely distributed in small amounts in the silver-gold fissure veins. Some of it is secondary, but it is in part probably primary also, for it occurs on the adit (1,400-foot) level of the Granite mine and is reported on good authority to have been found on the 2,200-foot level, where secondary enrichment of silver was ineffective.

Stalagmititic realgar was found by Weed and Pirsson[4] on Gibbon River in sinter now being deposited by hot springs, where realgar has formed under surface conditions. At Monte Cristo, Wash.,[5] realgar is found in arsenopyrite ores only in cracks and as crusts and is there everywhere secondary. In the Foggy tunnel, Goat Lake, Wash., according to Spurr,[6] realgar seems to have formed on broken rocks since drifts were opened. Realgar is found in considerable abundance at Mercur, Utah,[7] where arsenopyrite is not present nor is there any other source of arsenic sulphide mentioned. Realgar is therefore probably primary. It is absent in the oxidized zone, where it has altered to scorodite. Realgar is not mentioned in the arsenopyrite gold ores of California and at many other places where primary ore carries arsenopyrite. Realgar is reported with arsenopyrite near Mineral, Lewis County, Wash.

Orpiment, As_2S_3, is like realgar, comparatively rare. It is formed in sinter of hot springs at Yellowstone Park and is reported as a secondary mineral at Mercur, Utah. At Philipsburg, Mont.,[3] it is found here and there in the silver-gold lodes, where it is, in part at least, a secondary mineral after arsenopyrite.

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[1] Crawford, R. D., A preliminary report on the geology of the Monarch mining district: Colorado Geol. Survey Bull. 1, p. 27, 1910.

[2] Curtis, J. S., Silver-lead deposits of Eureka, Nev.: U. S. Geol. Survey Mon. 7, p. 54, 1884.

[3] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 153, 1913.

[4] Weed, W. H., and Pirsson, L. V., Occurrence of sulphur, orpiment, and realgar in the Yellowstone National Park: Am. Jour. Sci., 3d ser., vol. 42, p. 403, 1891.

[5] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 837, 1901.

[6] Idem, p. 854.

[7] Spurr, J. E., Economic geology of the Mercur district, Utah: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 428, 1895.

Gersdorffite, NiAsS, and *chloanthite*, $NiAs_2$, are discussed on page 466.

Cobaltite, CoAsS, and *smaltite*, $CoAs_2$, are discussed on pages 470–471, and the silver-arsenic salts on page 262.

Tennantite, $4Cu_2S.As_2S_3$, is discussed on page 280.

Tetrahedrite, according to Dana, invariably contains arsenic, and should be mentioned here. (See p. 278.)

Enargite (see p. 197) is one of the most important arsenic-bearing minerals. It is generally primary, but at Butte it has been considered secondary by some, and recently Ray has found it replacing iron sulphide at considerable depth, where he regards it as primary. Enargite might form, however, by downward enrichment in alkaline solutions, for several arsenic minerals are soluble in dilute alkaline waters,[1] and pyrite, which is more soluble in alkaline than in acid solution, could under these conditions be replaced. (See p. 124.)

Arsenopyrite, FeAsS, is a constituent of many pegmatite veins and has been noted as a contact-metamorphic mineral. It is a primary mineral in deposits of the deep zone and in some lodes formed at moderate depths. In such deposits it commonly carries gold. It is not known as a secondary constituent of ores enriched by descending sulphate solutions.

Arsenopyrite is found in many gold veins of California, Colorado, Montana, and other western States. It is common also in the Appalachian region. In the arsenical silver veins of Cobalt, Ontario, it is comparatively rare but has been noted, for example, in the Buffalo mine.[2] It is reported also on the Big Dan and Little Dan claims, near Temegami.[2] At Philipsburg, Mont., it is an abundant primary mineral in the lower zones of silver-bearing fissure veins, where it carries gold.[3] It is also present, though less abundant, in the Cable mine. Arsenopyrite is contemporaneous with pyrrhotite at Monte Cristo, Wash.[4]

At Brinton, Floyd County, Va., arsenopyrite deposits in mica schist have been mined and the ore has been calcined for white arsenic.[5] In these deposits the arsenopyrite near the surface loses its bright color, becomes black, is etched, and finally is dissolved.

Löllingite, $FeAs_2$, is a constituent of some pegmatites and is found in some quartz veins. It is probably everywhere primary.

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[1] Grout, F. F., On the behavior of cold acid sulphate solutions of copper, silver, and gold with alkaline extracts of metallic sulphides: Econ. Geology, vol. 8, p. 427, 1913.

[2] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, p. 20, 1913.

[3] Emmons, W. H., and Calkins, F. C., op. cit., p. 154.

[4] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 836, 1901.

[5] Hess, F. L., The arsenopyrite deposits of Brinton, Va.: U. S. Geol. Survey Bull. 470, p. 209, 1912.

ANTIMONY.

PRINCIPAL ANTIMONY MINERALS.

The names and chemical composition of the principal antimony minerals are given below:

Native antimony	Sb.
Stibiconite	$2SbO_2.H_2O$.
Cervantite	Sb_2O_4.
Senarmontite	Sb_2O_3.
Valentinite	Sb_2O_3.
Bindheimite	$Pb_2Sb_2O_5+aq.$
Tetrahedrite	$4Cu_2S.Sb_2S_3$.
Pyrargyrite	Ag_3SbS_3.
Stephanite	Ag_5SbS_4.
Polybasite	Ag_9SbS_6.
Bournonite	$PbCuSbS_3$.
Jamesonite	$Pb_2Sb_2S_5$.
Stibnite	Sb_2S_3.

OCCURRENCE AND RELATIONS OF ANTIMONY MINERALS.

Antimony closely resembles arsenic in its chemical relations, but it is less readily oxidized and is commonly more basic than acid forming. Unlike arsenic, it forms a sulphate, $Sb_2(SO_4)_3$. The simple sulphate is unstable in water, however, and is unknown in ore deposits. It hydrolyzes as follows:

$$Sb_2(SO_4)_3+2H_2O=Sb_2O_2SO_4+2H_2SO_4.$$

The chloride also is readily hydrolyzed in feebly acid or in neutral solution. As shown by H. C. Cooke, antimony sulphide is very slowly attacked by sulphuric acid and also even in presence of ferric sulphate. Native antimony is probably more common than native arsenic in nature. In the electromotive series (p. 112) it stands between hydrogen and copper. Three oxides are known—senarmontite and valentinite, Sb_2O_3, and cervantite, Sb_2O_4. There is also the hydrous oxide stibiconite. All of these, as well as native metal, are formed by oxidation or reduction of sulphides or other antimony compounds. Of the oxides of antimony the trioxide, Sb_2O_3, is generally basic; the tetroxide, Sb_2O_4, is the most stable oxide and is neither acidic nor basic; and the pentoxide, Sb_2O_5, combines with bases and is acid-forming exclusively.

From an acid solution in which antimony is dissolved either as sulphate or as chloride hydrogen sulphide or alkaline sulphides precipitate antimony sulphide by the reaction

$$2SbCl_3+3H_2S=Sb_2S_3+6HCl.$$

From its position in the Schuermann series antimony sulphide should replace sulphides of lead, zinc, nickel, cobalt, iron, and arsenic; but

I can find no examples of stibnite replacing these sulphides, though Hintze[1] mentions pseudomorphs of bournonite after galena and siderite. Very commonly, however, antimony enters secondary sulphides with other metals, particularly with silver. The waters of mines that contain considerable antimony as sulphide carry only a little antimony, generally only a trace. It has been recognized, however, in acid waters at Philipsburg and Butte, Mont., and elsewhere but only in very small quantities.

As already stated, the tendency of antimony sulphate to hydrolyze and form insoluble oxide prevents its extensive migration in weakly acid or neutral sulphate solution. Hydrochloric acid dissolves the sulphide very readily; but an oxidizing agent, like ferric salt, will precipitate antimony oxide. There is no soluble carbonate. Thus the chemical relations, as well as geologic occurrences, indicate that the metal is not highly mobile in the acid solutions of superficial weathering zones. Antimony sulphide is decomposed, but, like lead sulphide, it goes into solution very slowly.

Stibnite is much less soluble than sphalerite. In Arkansas[2] the antimony-lead ores are rather pure oxides or sulphides of antimony or lead for 40 to 115 feet from the surface, below which sphalerite comes in.

Silver, like zinc, appears to be leached out of antimony-silver ores. At Altar, Sonora, Mexico, even in a deposit where cerargyrite forms, the silver increases in value downward in antimony oxide ores.

As shown by Grout,[3] stibnite, which reacts very slowly in solutions of sulphuric acid, is one of the most reactive minerals in alkaline solutions. Of the common natural sulphides, its reactivity is exceeded only by that of orpiment when treated with a 1 per cent solution of alkaline carbonates or hydroxides. With these alkalies it forms double salts, like $Na_2S.Sb_2S_3$, which readily precipitate silver and copper from their solutions. Thus probably are formed the sulphantimonates pyrargyrite, stephanite, and other common secondary minerals.

Native antimony, like native arsenic, is comparatively rare and is probably invariably secondary. Large masses weighing as much as 1 ton are found with stibnite, valentinite, and kermesite in Prince William Parish, York County, New Brunswick.[4] Dana[5] mentions an occurrence in Kern County, Cal., and several others in Europe and Latin America.

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[1] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 1127.

[2] Hess, F. L., The Arkansas antimony deposits: U. S. Geol. Survey Bull. 340, p. 251, 1908.

[3] Grout, F. F., op. cit., p. 427.

[4] Blake, W. P., Antimony: U. S. Geol. Survey Mineral Resources, 1883–84, p. 644, 1885.

[5] Dana, J. D., System of mineralogy, 6th ed., p. 12, 1892.

Stibiconite, $Sb_2O_4.H_2O$, antimony ocher, is commonly an alteration product of stibnite. At Altar, Sonora, Mexico,[1] in an arid climate, veins in quartzite and limestone, from 4 to 20 feet wide, and explored to depths of 30 feet, contain antimony oxide ore that has the chemical composition of stibiconite, the hydrous oxide. Blake,[2] describing this deposit later than Cox, states that the quantity of silver, which was present partly as chloride, increased with increase of depth, indicating that the antimony oxide was the capping of an antimony silver ore. Stibiconite is probably a constituent of partly oxidized stibnite found near Red Butte, Humboldt County, Nev.

Cervantite, Sb_2O_4, is likewise a superficial alteration product of antimony minerals and is probably the most stable oxide.[3]

In the antimony deposits of Arkansas,[4] cervantite is an oxidation product of stibnite. It is reported also in the Wood River district, Idaho.[4]

Senarmontite, Sb_2O_3 (octahedral), and *valentinite*, Sb_2O_3 (monoclinic), are both alteration products of stibnite. According to Blake these are found with stibnite in the ores of Coyote Creek in southern Utah.[5]

Valentinite is found also as an oxidation product of stibnite in ores of Prince William Parish,[6] York County, New Brunswick.

Stibnite, Sb_2S_3, which is the commonest antimony mineral, is practically unknown in contact-metamorphic deposits, and it is rare in veins formed at high temperatures and pressures. Its occurrence is fairly common in veins formed at moderate and at shallow depths. Antimony sulphide (metastibnite) has been noted also at the orifices of hot springs.[7] Lindgren[8] found crystals of stibnite at Steamboat Springs, Nev., which had formed on gravels at depths not more than 30 feet. There is little if any evidence that stibnite is a secondary mineral formed by downward enrichment.

Stibnite is found in numerous veins in west-central Arkansas,[9] where it is associated with jamesonite, galena, sphalerite, and other minerals. It is found in ores of Bradshaw Mountains, Yavapai

[1] Cox, E. T., The discovery of oxides of antimony in extensive lodes in Sonora, Mexico: Am. Jour. Sci., 3d ser., vol. 20, p. 423, 1880.

[2] Blake, W. P., op. cit., p. 645.

[3] Dana, J. D., System of mineralogy, 6th ed., p. 203, 1892.

[4] Hess, F. L., The Arkansas antimony deposits: U. S. Geol. Survey Bull. 340, p. 251, 1908.

[5] Blake, W. P., op. cit., p. 643. Richardson, G. B., Antimony in southern Utah: U. S. Geol. Survey Bull. 340, p. 254, 1908.

[6] Blake, W. P., op. cit., p. 644.

[7] Becker, G. F., Quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, p. 344, 1888.

[8] Lindgren, Waldemar, The occurrence of stibnite at Steamboat Springs, Nev.: Am. Inst. Min. Eng. Trans., vol. 36, p. 27, 1906.

[9] Hess, F. L., op. cit., p. 251.

County, Ariz., in quartz veins with gold. Commercial quantities were found in a gold quartz vein in San Emigdio Canyon, Kern County, Cal.[1] Small quantities are present in many districts in Colorado, California, and New Mexico. It is abundant in the primary silver-gold ores of the Granite-Bimetallic lode, near Philipsburg, Mont.[2] It is found also at Eureka, Nev.

At Coyote Creek,[3] southern Utah, large "kidneys" and layers of stibnite and its oxidation products have been mined from flat-lying deposits in sandstone and conglomerate. Many of the layers are approximately parallel to bedding, and there is little gangue.

Small radiating crystals of stibnite are found also at Mercur, Utah, where it is probably primary.[4] At Monte Cristo, Wash., stibnite is found intergrown with realgar, which Spurr[5] regards as secondary. It generally occurs as free crystals lining druses.

On preceding pages discussions may be found of jamesonite, bindheimite, tetrahedrite, pyrargyrite, stephanite, polybasite, and bournonite.

BISMUTH.

PRINCIPAL BISMUTH MINERALS.

The names and chemical composition of the principal bismuth minerals are given below:

Native bismuth	Bi.
Bismite, bismuth ocher	$Bi_2O_3.3H_2O$.
Bismutite	$Bi_2O_3.CO_2.H_2O$?
Bismutosphærite	$2Bi_2O_3.Bi_2(CO_3)_3$.
Bismuthinite	Bi_2S_3.
Tetradymite	$Bi_2(Te,S)_3$.
Cosalite	$Pb_2Bi_2S_5$.

SOLUBILITIES OF SOME BISMUTH COMPOUNDS.

The chloride and the sulphate of bismuth are hydrolyzed in water and even in dilute acid solutions to insoluble compounds; the carbonate has exceedingly low solubility. Therefore the metal is not readily transported by cold mineral waters or concentrated by processes of sulphide enrichment.

OCCURRENCE AND RELATIONS OF BISMUTH MINERALS.

Although bismuth forms compounds in which it is trivalent, quadrivalent, and quinquivalent, it is in its natural compounds trivalent.

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[1] Blake, W. P., op. cit., p. 641.

[2] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 153, 1913.

[3] Richardson, G. B., op. cit., p. 254.

[4] Spurr, J. E., Economic geology of the Mercur mining district, Utah: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 391, 1895.

[5] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 837, 1901.

It is closely allied to arsenic and to antimony. Arsenic, however, is mainly a nonmetal acid-forming element; antimony is both acid forming and base forming; bismuth is base forming. As its position is below hydrogen and between antimony and arsenic in the electromotive series, the native metal is relatively stable. Unlike antimony and arsenic, native bismuth is primary. Next to mercury its sulphide is most insoluble in water, and if bismuth were dissolved it should replace sulphides of other metals in processes of superficial alteration, but occurrences of pseudomorphs of bismuth sulphides after other sulphides are rare. J. A. Bancroft[1] states that a pseudomorph of bismuthinite after molybdenite was collected on Kewagama River, Quebec, which, however, he thinks was formed by the introduction of later exhalations or solutions, presumably from a deep source.

Bismuth forms a sulphate, but this hydrolyzes in water or in weak acid and is rare or unknown in ore deposits. Unlike arsenic and antimony, bismuth forms stable carbonates, and it forms oxides corresponding to those of antimony. Atelsite, the arsenate of bismuth, $H_2Bi_3AsO_8$, is very rare, as is also the silicate eulytite, $Bi_4Si_3O_{12}$. In view of the facts that bismuth is not strongly basic and its salts are therefore easily hydrolyzed, and that silica is a very weak acid, it is probable that the silicate is primary. The oxide bismite is secondary. The sulphide of bismuth is much less soluble than that of arsenic or antimony. Bismuth does not readily form a soluble complex alkaline sulphide and its minerals are not affected by dilute alkalies; therefore it does not readily combine with sulphur to form the complex secondary copper and silver sulphosalts corresponding to those of arsenic and antimony. Cosalite, a lead-bismuth sulphide, is of uncertain constitution. Analyses vary considerably, and it may be a so-called "solid solution" rather than a mineral with definite formula. It is probably invariably primary.

Native bismuth, unlike arsenic and antimony, is not exclusively a secondary mineral formed in the zone of oxidation. Most of its occurrences are primary. Native bismuth, bright metallic with cleavage, is found in lepidolite in pegmatite veins of Rincon, San Diego County, Cal.[2] Bismuth occurs also in practically all the veins of Cobalt, Ontario.[3] It is found also in the Boss Tweed mine and in the Emerald mine in the Tintic district, Utah.[4] On the 500-foot level of the Emerald mine a fragment of limestone coated with

[1] Bancroft, J. A., Report on the geology and mineral resources of Keekeek and Kewagama lakes region: Quebec (Province) Mines Branch Rept. on mining operations during 1911, p. 189, 1912.

[2] Rogers, A. F., Minerals from the pegmatite veins of Rincon, San Diego County, Cal.: School of Mines Quart., vol. 31, p. 208, 1910.

[3] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, p. 15, 1913.

[4] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 703, 1899.

delicate crystals of native bismuth was found. Near Trumbull, Conn.,[1] native bismuth in a quartz vein is associated with marcasite, sphalerite, galena, and arsenopyrite.

It is apparently primary in the bismuth deposits of Johanngeorgenstadt,[2] Saxony, and in numerous tin and tungsten veins in the Erzgebirge and in Bolivia.

On the Mole Tableland, in northern New South Wales, bismuth is found in pegmatites or pegmatite veins, with bismuthinite, smaltite, wolframite, monazite, topaz, tourmaline, beryl, fluorspar,[3] and lithium mica.[4]

Native bismuth is found in veins with bismuthinite and cassiterite in Silent Grove Parish, northern New South Wales;[5] with pyrite and arsenopyrite at Adelong; with wolframite, arsenopyrite, and molybdenite at Ding Dong; and in veins at other places in New South Wales.[6] At Kingsgate a mass weighing 400 pounds was found.[7] Native bismuth occurs with bismuthinite and bismuth carbonate, copper minerals, tourmaline, pyrite, molybdenite, and wolframite at Lintons, Victoria.[8] Native bismuth is found in many of the tin veins of Cornwall.[9]

Bismite, $Bi_2O_3.3H_2O$, is probably everywhere an oxidation product. It is found in several mines of Goldfield, Nev., where it is associated with limonite and is confined to the oxidized zones. Glittering scales on walls and cavities are frequently associated with such ore. It is found also as pseudomorphs after bismuthinite. Although bismuthinite is apparently the original sulphide in the ores, the bismuth has evidently migrated somewhat, since, as is shown by Ransome,[10] bismite scales and crystals do not everywhere occupy bismuthinite forms. At Rincon, Cal.,[11] microscopic crystals of bismite are associated with bismuth as an oxidation product.

At Hilltop, Nev., 14 miles southeast of the Battle Mountain mine, bismuthinite is found in rich gold ore in quartzite. On oxidation

[1] Hobbs, W. H., The old tungsten mine at Trumbull, Conn.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 13, 1901.

[2] Viebig, W., Die Silberwismuthgänge von Johanngeorgenstadt in Erzgebirge: Zeitschr. prakt. Geologie, vol. 13, p. 102, 1905.

[3] Andrews, E. C., New South Wales Dept. Mines Ann. Rept., 1904, p. 143, Sydney, 1905.

[4] Carne, J. E., The tungsten mining industry in New South Wales: New South Wales Geol. Survey Mineral Resources 15, pp. 68–71, 1912.

[5] David, T. W. E., Geology of the Vegetable Creek tin-mining field, New England district, New South Wales: New South Wales Geol. Survey Mem. 1, p. 168, Sydney, 1887.

[6] Pittman, E. W., The mineral resources of New South Wales, pp. 256–272, New South Wales Geol. Survey, 1901.

[7] Idem, p. 262.

[8] Baragwanath, W., Lintons (V.) wolfram lodes: Australian Min. Standard, vol. 48, p. 225, 1912.

[9] Collins, J. H., A handbook to the mineralogy of Cornwall and Devon, pp. 15–16, 1871.

[10] Ransome, F. L., Geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 123, 1909.

[11] Rogers, A. F., op. cit., p. 208.

near the surface, according to G. J. Young, the bismuthinite becomes incrusted with bismite.[1]

Collins[2] notes that bismite occurs in a number of Cornish tin mines, and Dunstan[3] lists bismite from the Burnett, Kennedy South, and Moreton districts of Queensland. Probably many of the Queensland mines carry bismite among the oxidized ores, but it is not readily separated from the other oxidized bismuth and associated minerals.

Bismutite, $Bi_2O_3H_2CO_3$, and *bismutosphærite*, $2Bi_2O_3.Bi_2(CO_3)_3$, are probably everywhere secondary. According to Hess,[4] bismuth carbonate ore is mined at Engle, N. Mex., where it is associated with copper carbonates and scheelite. It has been mined also at the Highland Mary mine at Leadville, Colo.[5] It has been found at Leadville associated with sulphides.[6] The anhydrous carbonate was determined also by Genth in material from Mount Antero,[7] Chaffee County, Colo., where it is probably an alteration product of bismuth sulphide.

At Willimantic, Conn., according to H. L. Wells,[8] bismutosphærite is pseudomorphous after bismuthinite, and is associated with garnet and albite. In this region crystals of the anhydrous carbonate also were noted. The anhydrous carbonate was found also in material from Portland, Conn. Bodenhender[9] describes a vein of bismuth carbonate in the Sierra de San Luis, Argentina. An analysis shows that the mineral contains also lime and manganese carbonates. A small vein of bismuth carbonate was found in the Jelm Mountains, Albany County, Wyo.[10]

Bismutite is found in the oxidized parts of most of the veins and pegmatites mentioned as carrying native bismuth and bismuthinite. Its common occurrence in the oxidized parts of the deposits indicates the insolubility and immobility of bismuth in the solutions that are formed in the oxidized zones of bismuth deposits.

In Queensland[11] oxidized bismuth minerals are found near Lappa Junction with cassiterite, wolframite, molybdenite, torbernite, and

[1] Young, G. J., oral communication.

[2] Collins, J. H., op. cit.

[3] Dunstan, B., Queensland mineral index and guide: Queensland Geol. Survey Pub. 241, p. 123, 1913.

[4] Hess, F. L., Bismuth: U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 714, 1909.

[5] Hess, F. L., Bismuth: U. S. Geol. Survey Mineral Resources, 1912, pt. 1, p. 1043, 1913.

[6] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 377, 1886.

[7] Genth, F. A., Contributions to mineralogy: Am. Jour. Sci., 3d ser., vol. 43, p. 189. 1892.

[8] Wells, H. L., Bismutosphærite from Willimantic and Portland, Conn.: Am. Jour. Sci., 3d ser., vol. 34, p. 271, 1887.

[9] Bodenhender, W., Wismuthspath in Gangform: Zeitschr. prakt. Geologie, vol. 7, p. 323, 1899.

[10] Darton, N. H., Blackwelder, Elliot, and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Laramie-Sherman folio (No. 173), p. 15, 1910.

[11] Dunstan, B., op. cit., pp. 128–130.

topaz; on the Walsh and Tinaroo fields and at Wolfram Camp with tin, tungsten, and molybdenum minerals, arsenopyrite, pyrite, and other bismuth minerals.

Considerable quantities of oxidized bismuth ore have been shipped from Huarancara, Peru. This ore has been reported to be an arsenate. Specimens show no arsenic, however, and the ore is probably bismutite, possibly accompanied by other oxidized bismuth minerals. The minerals, which were in a gossan, were slightly argentiferous. No unoxidized minerals were found, and the original mineral or minerals are unknown.[1]

Bismuthinite, Bi_2S_3, is, so far as known, a primary mineral. It was noted by the writer in a contact-metamorphic garnet zone at West Cananea mine, Sonora, Mexico, where it occurs intergrown with copper sulphides and heavy silicates. It is reported in the Granite district, Beaver County, Utah, with garnet and barite, a remarkable association of minerals.[2] It is common in sulphide ores formed at moderate and at shallow depths. At Goldfield, Nev., it is intergrown with free gold[3] and is regarded as a favorable indication of gold. It is also irregularly crystallized with quartz and pyrite. Stellate or sheaf-like forms are common in the Goldfield ores. In the San Francisco region, Utah, it was noted in ore from the St. Mary's mine.[4] Bismuth sulphide has been identified also at Leadville, Colo.[5] It occurs in considerable bodies of ore in the Boss Tweed mine, Tintic, Utah,[6] where it is associated with barite and quartz, and, as at Goldfield, has radial growths. It is associated with tetradymite in the Dolcoath mine[7] at Elkhorn, Mont. It has been reported also from the Jelm Mountains,[8] Albany County, Wyo.

Bismuth has been found in pegmatitic veins with molybdenite in the town of Cooper, 22 miles southwest of Calais, Maine.[9] Bismuthinite is associated with cassiterite, iron, antimony, arsenic, and silver sulphides, and traces of gold in the Llallagua and Uncia mines, Bolivia.[10] In Tasmania, near Wilmot,[11] it is found in the Shepherd

[1] Hewett, D. F., and Ferguson, H. G., oral communication.

[2] Dana, J. D., System of mineralogy, 6th ed., p. 38, New York, 1892.

[3] Ransome, F. L., Geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 111, 1909.

[4] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[5] Emmons, S. F., Geology and mining industry of Leadville, Colo.: U. S. Geol. Survey Mon. 12, p. 377, 1886.

[6] Tower, G. W., and Smith, G. O., Geology and mining industry of Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 703, 1899.

[7] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 460, 1901.

[8] Darton, N. H., Blackwelder, Eliot, and Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Laramie-Sherman folio (No. 173), p. 15, 1910.

[9] Hess, F. L., Some molybdenum deposits of Maine, Utah, and California: U. S. Geol. Survey Bull. 340, p. 233, 1908.

[10] Rumbold, W. R., Origin of the Bolivian tin deposits: Econ. Geology, vol. 4, pp. 352–357, 1909.

[11] Petterd, W. F., Catalogue of the minerals of Tasmania, pp. 28–29, Tasmania Dept. Mines, 1910.

and Murphy mine with cassiterite, wolframite, pyrite, fluorite, calcite, quartz, wollastonite, spodumene, hydrated mica and topaz. Beautiful crystals are reported in a quartz vein with wolframite and a little molybdenite, gold and silver on the adjoining All Nations claim. It occurs with native bismuth in amphibolite at Mount Ramsay;[1] it has been noted in tin mines at Heemskirk, Tasmania, and in the stanniferous granite of the Blue Tier. It is intimately associated with tetrahedrite and pyrite at Dundas, where it is mined.[1]

At Kingsgate,[2] New South Wales, numerous pipes of bismuth ore are found in granite. These contain near the surface the oxide, the carbonate, and some native bismuth. At depths bismuth sulphide and native bismuth are more abundant. The gangue is quartz, some of which incloses long needles of native bismuth and of bismuth sulphide. Associated minerals are arsenopyrite, wolframite, and molybdenite, with gold and silver.

Bismuth deposits are worked at Whipstick,[3] also in New South Wales, 500 miles away. They also are irregular cylindrical pipes in granite. The gangue minerals are coarse feldspar, quartz, and mica with a little garnet. Near the surface bismuth oxide and carbonate are found and at depths the sulphide is most abundant. Large masses of native bismuth, associated with white quartz, also are found in the deposits.

Tetradymite, $Bi_2(Te,S)_3$, is generally, if not exclusively, primary. In view of the rarity of the tellurides and of bismuth, the number of occurrences of tetradymite is noteworthy. It is present in many lode ores, particularly in those formed at moderate and shallow depths, and is reported from nine States of the Union.[4] Nowhere is it abundant. Although it is most common in deposits formed at moderate and shallow depths, it is reported also as found in garnetiferous rock at Dolcoath mine, Elkhorn, Mont.,[5] and it is probably present at Nevada City, Cal., where a small quantity of bismuth was found in the concentrates from the Providence mine.[6]

It is stated to occur at three places in Queensland and joseïte, another bismuth telluride, at a score of places.[7]

Cosalite, $Pb_2Bi_2S_5$, is a comparatively rare mineral. All known occurrences are probably primary. It has been noted in the San

[1] Petterd, W. F., Catalogue of the minerals of Tasmania, pp. 28–29, Tasmania Dept. Mines, 1910.

[2] Pittman, E. F., Mineral resources of New South Wales: New South Wales Geol. Survey, p. 259, 1901.

[3] Idem, p. 262.

[4] Sanford, Samuel, and Stone, R. W., Useful minerals of the United States: U. S. Geol. Survey Bull. 585, p. 246, 1914.

[5] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 460, 1901.

[6] Lindgren, Waldemar, The gold quartz veins of Nevada City and Grass Valley districts, Cal.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, p. 117, 1896.

[7] Dunstan, B., Queensland mineral index and guide: Queensland Geol. Survey Pub. 241, pp. 624, 944, Brisbane, 1913.

Francisco region, Utah, where, in the ore zone of the Cactus mine,[1] on the seventh level, it is contemporaneous with siderite and anhydrite.

Cosalite was found in the ore of the Yankee Girl mine near Silverton, Colo.[2] Near Loon Lake, in Stevens County, Wash.,[3] argentiferous cosalite is found in quartz veins in mica schist near granite. Associated minerals are hübnerite and galena. It has been noted at Parrot City and other camps of the La Plata Mountains, Colo.

VANADIUM.

The principal vanadium minerals are listed below:

Vanadinite	$PbClPb_4(VO_4)_3$.
Descloizite	$4(Pb,Zn)O.V_2O_5.H_2O$.
Dechenite	$(Pb,Zn)(VO_3)_2$.
Pucherite	$BiVO_4$.
Volborthite	$(Cu,Ca)(VO_3)_2.H_2O$.
Sulvanite	$3(Cu_2S)V_2S_5$.
Patronite	V_2S_5+nS.
Carnotite	$K_2O.2UO_3.V_2O_5.8H_2O$.
Tyuyamunite	$CaO.2UO_3.V_2O_5.8(?)H_2O$.
Uvanite	$2UO_3.3V_2O_5.15H_2O$.
Roscoelite	$AlV_2.KH_2.Si_3O_{10}$.

In the periodic system vanadium, with the rarer metals, tantalum and columbium, stands between the arsenic and chromium groups. The oxide, V_2O_5, reacts with bases to form vanadates. The metal is, however, only feebly base-forming and gives unstable salts. The vanadate behaves much like the phosphate and arsenate radicles and forms corresponding compounds. There is no native metal. In its geologic environments vanadium is more commonly associated with lead than with its near neighbors in the periodic system. It resembles uranium in its tendency to migrate. Vanadium is a common constituent of igneous rocks, particularly the basic ones, and is frequently found in sedimentary rocks.[4]

Very little is known concerning the behavior of vanadium compounds in dilute sulphate solutions. Vanadous sulphate, $VSO_4.7H_2O$, is said to be isomorphous with ferrous sulphate,[5] but it oxidizes more readily. Vanadium sulphate, $V_2(SO_4)_3$, with alkali sulphates, forms a soluble salt in acid solutions. Minasragrite, $V_2O_4.3SO_3.16H_2O$, or

[1] Butler, B. S., op. cit., p. 122.

[2] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colo.: U. S. Geol. Survey Bull. 182, p. 84, 1901.

[3] Bancroft, Howland, The ore deposits of northeastern Washington: U. S. Geol. Survey Bull. 550, p. 132, 1914.

[4] Hillebrand, W. F., Distribution and quantitative occurrence of vanadium and molybdenum in rocks of the United States: U. S. Geol. Survey Bull. 167, p. 49, 1910.

[5] Roscoe, H. E., and Schorlemmer, C., A treatise on chemistry, 4th ed., p. 913, London, 1907.

$(V_2O_2).H_2(SO_4)_3.15H_2O$,[1] a blue vanadium sulphate which forms upon the patronite of Minasragra, Peru, is easily soluble in water. Other readily soluble vanadium minerals are pascoite, $2CaO.3V_2O_5.11?H_2O$, an apricot-yellow mineral found at Minasragra,[2] in the Henry Mountains, and at other points in Utah,[3] and pintadoite,[4] $2CaO.V_2O_5.9H_2O$, found as a dark-green efflorescence at many places in the Utah uranium and vanadium field. Any of these soluble compounds could transport vanadium. The sulphide, patronite,[5] has been identified by Hewett[6] in a vein at Minasragra, Peru. The deposits are in Mesozoic sediments that are intruded by numerous dikes of eruptive rocks. The principal vanadium deposit occupies a fault fissure, and the mineral patronite is associated with coke and asphaltum. The carbon compounds occupy the walls and the sulphide the center of the vein. Oxidation yields green and brown oxides, which have been mined. In the oxidation process vanadium has been dissolved and reprecipitated in cracks of crushed shale near the deposits.

At San Rafael, Mendoza, Argentina,[7] an asphaltite carries vanadium. Vanadium occurs possibly as sulphide in asphaltites at Page, Okla., Palisade, Nev., and Yauli, Peru.[8]

Vanadinite, $PbCl.Pb_4(VO_4)_3$, is chiefly a secondary mineral. It is found at Lake Valley, N. Mex.,[9] and in the Sierra de los Caballos, N. Mex. Through a distance of 2 miles southward from Palomas Gap vanadinite, with calcite, fluorite, barite, quartz, and copper carbonates, occupies fissures in limestone containing brecciated country rock cemented by the ore. A zinc-bearing cuprodescloizite is present.[10] Crusts of vanadinite not more than one-sixteenth inch thick coat limestone. In the White Swan vein minute hairlike crystals form rosettes lining cavities in calcite from which galena was dis-

[1] Schaller, W. T., Four new minerals: Washington Acad. Sci. Jour., vol. 5, p. 7, 1915.

[2] Hillebrand, W. F., Merwin, H. E., and Wright, F. E., Hewettite, metahewettite, and pascoite, hydrous calcium vanadates: Am. Philos. Soc. Proc., vol. 53, pp. 49–53, 1914.

[3] Hess, F. L., and Schaller, W. T., Pintadoite and uvanite: Washington Acad. Sci. Jour., vol. 4, p. 579, 1914.

[4] Idem, pp. 577–578.

[5] Hillebrand, W. F., The vanadium sulphide, patronite, and its mineral associates from Minasragra, Peru: Am. Chem. Soc. Jour., vol. 29, p. 1019, 1907.

[6] Hewett, D. F., Vanadium deposits in Peru: Am. Inst. Min. Eng. Trans., vol. 40, p. 274, 1909.

[7] Kyle, J. J. J., On a vanadiferous lignite found in the Argentine Republic, with analysis of the ash: Chem. News, pp. 211–212, 1892. Although Kyle calls the substance lignite his analyses show that it is asphaltite.

[8] Hewett, D. F., Vanadium deposits in Peru: Am. Inst. Min. Eng. Trans., vol. 40, p. 280, 1910. Richardson, Clifford, Grahamite, a solid native bitumen: Am. Chem. Soc. Jour., vol. 22, pp. 1047–1048, 1910. Gives also a number of other localities at which asphaltites carrying vanadium are found.

[9] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 279, 1910.

[10] Hess, F. L., Vanadium in the Sierra de los Caballos, N. Mex.: U. S. Geol. Survey Bull. 530, p. 158, 1913.

solved. The vanadinite is also distributed as minute crystals in calcite.[1]

Vanadinite is found[2] in the Organ Mountains, Dona Ana County, 35 miles east of Las Cruces; at Bayard, Silver City, Mimbres, Fierro, and 10 miles west of Cooks, Grant County; at Kelly, Socorro County; and other places in New Mexico. In Arizona vanadinite is found at Willcox; on the Orizaba and other claims, 23 miles south of Casa Grande; at Humboldt and Constellation, Yavapai County; at Globe, Gila County, with descloizite and cuprodescloizite; at Gold Basin and Signal, Mohave County; at Big Bug, Black Prince mine, Pioneer district; at the Royal Dane claim, 7 miles southwest of Oracle, Pinal County; and at other places. In California it is found at Camp Signal, San Bernardino County, with cuprodescloizite and probably other vanadium minerals. In Nevada it is found at Crescent and Searchlight, Clark County, and at other places. In Montana, it is found in the Rothschild mine, 27 miles northwest of Dillon. In Colorado it is found in Montrose and San Miguel counties.[3] It has been found in small quantity in Pennsylvania, New York, and other States. In Spain it has been worked as a source of vanadium.[4] It is found and has been exploited in the provinces of Cordoba and San Luis, Argentina, where it is accompanied by descloizite and psittacinite.[5] In Algeria[6] vanadinite is found near Saïda, Oran, with endlichite (the arsenical vanadinite), descloizite, and cerusite; at Djebel Grouz, Constantine, with descloizite, mimetite and pyromorphite; and at Sidi Roumain. In Tunis[7] it is found near Souk-el-Khemis; in the French Congo[8] in Djoué; in Tasmania,[9] at Bell's Reward mine, and, with endlichite, at Heazlewood and in the Magnet mine.

In Mexico vanadinite has been shipped from the Aurora mine, near Cuchillo Parado on Conchos River, in northeast Chihuahua, where it occurs with wulfenite and argentiferous galena. Vanadium was discovered by Del Rio in vanadinite from Zimapan, in 1801, though later he concluded that it was chromium and so stated in 1804.

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[1] Hess, F. L., op. cit., p. 159.

[2] Except where otherwise stated, the references to the occurrences below are supplied by Mr. F. L. Hess.

[3] George, R. D., Common minerals and rocks, their occurrence and uses: Colorado State Geol. Survey Bull. 6, p. 181, Denver, 1913.

[4] Nicolardot, Paul, Industrie des métaux secondaires et des terres rares: Encyc. sci., p. 139, Paris, 1908.

[5] Kyle, J. J. J., op. cit., p. 212

[6] Lacroix, A. Minéralogie de la France et de ses colonies, vol. 4, pp. 411–412, Paris, 1910.

[7] Idem, p. 412.

[8] Idem, vol. 5, p. 82, 1913.

[9] Petterd, W. F., Catalogue of the minerals of Tasmania, pp. 68, 196, Tasmania Mines Dept., 1910.

Vanadium, like phosphorus, is found in considerable abundance in ashes of some plants, and it is probably present in some bones, but if so in amounts much subordinate to phosphorus. L. J. Spencer[1] describes an occurrence of vanadinite in Rhodesia in a huge cave containing abundant bones and some implements of early man. The bones are incrusted by calamine which in turn is incrusted by botryoidal vanadinite, which is covered with crystals of hopeite. In a neighboring deposit galena and sphalerite are associated minerals and in it several tons of descloizite were found, mixed with limonite, pyromorphite, and hopeite.

In view of the relations above mentioned, four sources of vanadium in mineral waters are possible—(1) igneous rocks, the average of which carry, according to Clarke,[2] 0.17 per cent vanadium; (2) sediments derived from igneous rocks; (3) primary ore minerals such as patronite; (4) organic salts derived from plants and animals.

Descloizite (vanadate of lead and zinc) occurs in the Elkhorn mine, Montana,[3] as thin, mossy, dull yellow-green crusts of minutely crystalline surface, coating cavities in a deposit of amorphous silica. It is found on the hanging-wall ore body of the 1,300-foot level. It is abundant in a mine at Broken Hill, Rhodesia, where it is associated with quartz, limonite, and galena.[4]

Cuprodescloizite is found in considerable quantity and in beautiful development, with copper minerals, at Bisbee, Ariz. It is also found at Goodsprings, Nev., and Camp Signal, San Bernardino County, Cal. As noted above, both descloizite and cuprodescloizite are frequently found with vanadinite.

Dechenite, a variety of descloizite, according to Ricketts,[5] has been found at Leadville, in very small quantity in the Evening Star mine. It occurs as an incrustation on a siliceous gangue. When thick the coatings have deep brick-red color, and surfaces 6 inches across have been found completely covered with it.

Tyuyamunite, $CaO.2UO_3.V_2O_5.8(?)H_2O$, is the lime carnotite. From recent researches made by Schaller in the laboratory of the United States Geological Survey it appears that both carnotite and tyuyamunite normally carry 8 molecules of water, so that they are in line with the other minerals of the uvanite group, such as autunite and torbernite.

Uvanite, $2UO_3.3V_2O_5.15H_2O$, is now being produced commercially in southwestern Colorado for its radium content; the vanadium is saved as a by-product.

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[1] Spencer, L. J., On hopeite and other zinc phosphates and associated minerals from Broken Hill, northwestern Rhodesia: Mineralog. Mag., vol. 15, p. 3, 1908.

[2] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 27, 1916.

[3] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 467, 1901.

[4] Spencer, L. J., op. cit., p. 31.

[5] Ricketts, L D., The ores of Leadville, p. 29, Princeton, 1883.

Roscoelite.—Near Placerville, Colo.,[1] roscoelite, together with a little carnotite, cements grains of quartz sand of the La Plata. (See fig. 27.) In the Dolores formation, 1½ miles northwest of Placerville,[2] a vein which occupies a fault fissure carries some vanadium and some uranium. (See p. 434.) Azurite, malachite, chalcopyrite, chalcocite, molybdic ocher, molybdenite, galena, erythrite, autunite, gold, silver, and vanadium also occur in the vein, and here and there on the footwall side there are irregular lenses of an asphaltic material. A limestone near the vein on the hanging-wall side has been recrystallized, probably by solutions that brought in chromium mica, and the calcite granules are coated with mariposite. At Big Bear Creek, near Vanadium (Newmire), there are veins of roscoelite.[3]

Roscoelite at many places accompanies rich gold ores. It occurs at Cripple Creek, in the Mary McKinney mine, with quartz, fluorite, and calaverite.[4] In similar association it is known also in the Stuckslager mine, Cal., and at Placerville, both in Eldorado County; in eastern Oregon, near Sumpter, and in the Kalgoorlie mines, in Western Australia.

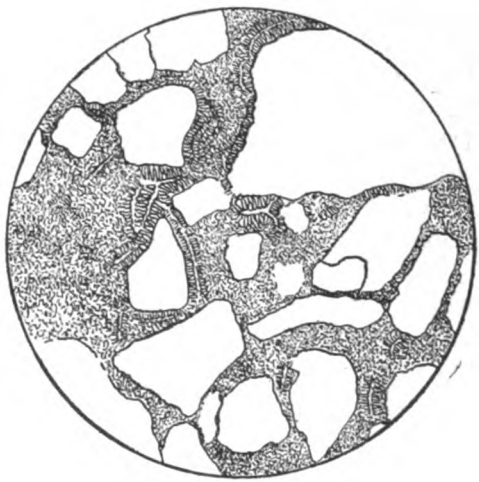

FIGURE 27.—Section of sandstone having wide pore spaces filled with roscoelite, partly radial. White space, quartz; shaded area, roscoelite. Enlarged about 225 diameters. After F. L. Hess.

At Richardson, Utah, vanadium and uranium minerals are found in sandstone. The deposits are chiefly compounds of vanadium, including vanadio-arsenates of copper, barium, and calcium. These occur as aggregates of small crystals grouped parallel or radiating in sheaves or wreaths.[5]

Vanadium is found in many deposits in the region along Dolores River, Paradox Valley, and northward to Gateway, Colo., La Sal Mountains, East Canyon, San Rafael Swell, and Henry Mountains, Utah.[6] Although most of these are known principally as carnotite

[1] Ransome, F. L., and Hillebrand, W. F., On carnotite and associated vanadiferous minerals in western Colorado: U. S. Geol. Survey Bull. 262, p. 14, 1905.

[2] Hess, F. L., Notes on the vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, p. 142, 1913.

[3] Hess, F. L., written communication.

[4] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 54, 1906.

[5] Boutwell, J. M., Vanadium and uranium in southeastern Utah: U. S. Geol. Survey Bull. 260, p. 205, 1905.

[6] Hess, F. L., A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, vol. 9, p. 675, 1914.

deposits, all contain vanadium minerals in excess of the uranium minerals. They are discussed on page 433.

CHROMIUM.

The principal chromium minerals are stated below:

Crocoite	$PbCrO_4$.
Chromite	$FeCr_2O_4$.
Picotite	$(Mg,Fe)O(Cr,Al)_2O_3$.
Chrome mica	$(Al,Cr)_2KH_2Si_3O_{12}$.

At 25° C. 1,000 cubic centimeters of water dissolves 243.9 grams of chrome alum, chromium potassium sulphate, $K_2Cr_2(SO_4)_4.24H_2O$. Both chromous sulphate, $CrSO_4.7H_2O$, and chromic sulphate, $Cr_2(SO_4)_3.18H_2O$, are soluble. At 0° C. 1,000 grams water dissolves 123.5 grams of chromous sulphate. The chromic salt is more soluble; 1,000 grams water dissolves 1,200 grams of chromic sulphate. The chloride, $2CrCl_3.13H_2O$, also is soluble. At 15° C. 1,000 grams water dissolves 1,300 grams of chromic chloride. At 18° C. 1,000 grams of water dissolves 0.0002 gram lead chromate, $PbCrO_4$.[1]

The elements chromium, molybdenum, tungsten, and uranium, which occupy exclusively the left side of the seventh column of the table showing the periodic classification of the elements, are comparable in chemical and geologic activities. Chemically, as acid-forming elements, they are closely related also to sulphur, selenium, and tellurium, tabulated on the right side of the same column. Like sulphur, they form trioxides, CrO_3, MoO_3, WO_3, and UO_3, and all have acids, like sulphuric acid, and corresponding salts. All these elements are thus hexavalent, though in other compounds they show lower valences also. Molybdenum and tungsten do not form bases.

In their geologic occurrences these metals show associations corresponding to their chemical relations. None are found free as natural minerals; the first two, chromium and molybdenum, are common primary constituents of igneous rocks; all occur in pegmatite veins; and the minerals of molybdenum, tungsten, and uranium are not very rare in metalliferous veins. Chromium is stable in its deposits; molybdenum and tungsten show slight transportation, and uranium salts are migratory.

Very similar are the compounds pyromorphite, the lead chlorphosphate; mimetite, the lead chlorarsenate; vanadinite, the lead chlorvanadate; and chromiferous mimetite. Uranium trioxide forms a similar group of nearly related phosphates, arsenates, and vanadates.

Chromite, $FeCr_2O_4$, including the aluminous and magnesian varieties, is the only ore of chromium. It is a rock-making mineral

[1] Kohlrausch, P., cited in Landolt-Börnstein, Physikalisch-chemische Tabellen, p. 491, Berlin, 1912.

and is found in basic rocks such as peridotite and serpentine derived from them. (See fig. 28.) In this association its primary occurrences are like those of nickel and cobalt. It is rare in contact-metamorphic deposits but is not unknown in them. It segregates in its deposits by magmatic differentiation.[1] Chromite is one of the most resistant minerals to weathering, and it commonly accumulates in gravels.[2] Although the sulphates and chlorides are soluble, the mineral chromite is very insoluble. Chromium minerals in sulphide ores might dissolve more readily, particularly in presence of ferric sulphate.

Chrome mica occurs sparingly in some mineral veins. The other minerals are relatively unimportant. The sulphide daubréeite, $FeS.Cr_2S_3$, is unknown, except in some meteoric irons. Chromium is very rare in sulphide ores and little is known of its behavior under weathering in such surroundings. Knoxvillite and redingtonite are hydrous basic chromium sulphates found in the Redington mercury deposits at Knoxville, Cal.

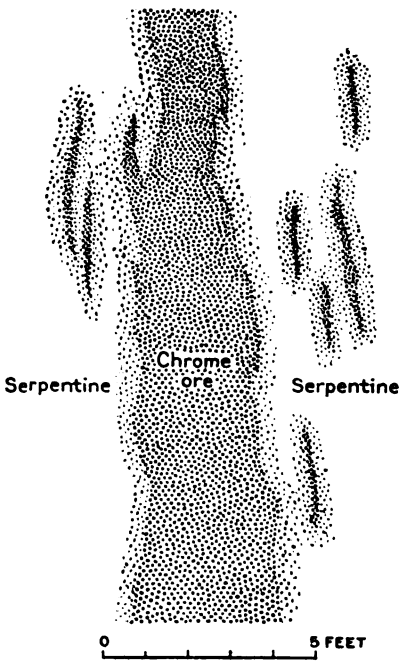

FIGURE 28.—Vertical section through a lenticular pocket of chrome ore south of Morro Creek, 12 miles northeast of San Luis Obispo, Cal. After E. C. Harder.

Crocoite, $PbCrO_4$, the lead chromate, is a rare mineral found in certain deposits in the Urals, in Hungary, and at Dundas, near Zeehan, Tasmania. At some of these places it occurs in quartz veins. There is also a basic lead chromate, phœnicite, $3PbO.2CrO_3$, and a phosphochromate of lead. These compounds, which are probably all secondary, illustrate the natural groupings of salts of chromium with those of sulphur and molybdenum in chemical action. Chromium was first identified from lead chromate. In the Magnet mine, near Dundas, Tasmania, chromiferous cerusite (lead carbonate with lead chromate) is found with chromiferous mimetite and crocoite.[3]

[1] Vogt, J. H. L., Zur Classification der Erzvorkommen: Zeitschr. prakt. Geologie, vol. 3, p. 384, 1894. Pratt, J. H., The occurrence, origin, and chemical composition of chromite: Am. Inst. Min. Eng. Trans., vol. 29, p. 17, 1899.

[2] Harder, E. C., Some chromic deposits of western and central California: U. S. Geol. Survey Bull. 430, p. 167, 1910.

[3] Petterd, W. F., Report of the Secretary of Mines for half year ending December 31, 1903, p. 76, Tasmania, 1904.

These minerals are associated with limonite, occur in fractures and vugs in the gossan, and are doubtless secondary. They are reported to appear in the deposit near a serpentine footwall. Crocoite is found in the Vulture district, Arizona, associated with wulfenite and vanadinite. It is suggested that it gives the bright-red color to some wulfenites.[1]

MOLYBDENUM.

The principal molybdenum minerals are listed below:

Wulfenite	$PbMoO_4$.
Powellite	$CaMoO_4.Ca(Mo,W)O_4$.
Molybdite	MoO_3.
Molybdic ocher	$Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$.
Ilsemannite	$MoO_3.4MoO_3$.
Molybdenite	MoS_2.

Molybdenum, as stated above, is chemically related to chromium and tungsten. It is a common constituent of igneous rocks and, unlike chromium, it occurs commonly in both acidic and basic rocks. Although molybdenite is found in many varieties of rocks, both siliceous and basic,[2] it is usually found in the more quartzose rocks in pegmatites and in quartz veins. Like tungsten, it forms a moderately stable trioxide, and in this respect is unlike chromium and sulphur. The trioxide, MoO_3, is soluble in cold water to the extent of 1.87 grams in 1,000 grams of water. With water it must form some molybdic acid, and on neutralization of the solution the molybdates of any bases present, such as those of calcium, lead, and iron, would be precipitated.

The only primary molybdenum mineral known is the sulphide, molybdenite. Its oxidation products include molybdite, molybdic ocher, ilsemannite, and powellite. Wulfenite is probably a decomposition product of molybdenite and galena. Although these secondary minerals are not uncommon in deposits carrying molybdenum, they seldom form in great abundance. As no large concentrations are known molybdenum is probably not very mobile in alteration. Molybdenite immersed in hydrochloric and in sulphuric acid after one month showed no loss, and neither ferric sulphate nor ferric chloride increased its solubility. Since molybdenite alters it must be somewhat soluble in ground waters, but I do not know the nature of its solvents.

Wulfenite, lead molybdate, $PbMoO_4$, is a product of alteration formed in oxidized ores. It is generally associated with limonite and occurs as bright crystals that line open cavities. At Eureka,

[1] Guild, F. N., The mineralogy of Arizona, p. 85, Easton, 1910.

[2] Crook, A. R., Molybdenite at Crown Point, Wash.: Geol. Soc. America Bull., pp. 284, 285, vol. 15, 1904.

Nev.,[1] in the ores of Ruby Hill, wulfenite is very common. It occurs as aggregates of fine tabular crystals coating nodules of lead sulphate and carbonate that have altered from galena. Minute crystals also are disseminated through the ore. Wulfenite is found coating crystals of galena in ores of the Hawkeye mine in the Monarch district, Colorado.[2] In the Harrington-Hickory mine, San Francisco region, Utah, wulfenite is an important constituent of some of the ores. In the Horn Silver mine, according to Butler,[3] cores of galena are surrounded by wulfenite. Wulfenite has been found also at Alta, Utah;[4] Stephenson-Bennett mine, Organ, N. Mex.; near Palomas Gap, in the Sierra de los Caballos, N. Mex.; at the Mammoth mine, Oracle, Ariz.; and in the Yuma mine, 14 miles northwest of Tucson, Ariz. The last four districts named are reported to be commercial sources of wulfenite. It is noteworthy that wulfenite is not found in association with molybdenite in these or other districts, although the molybdenum mineral from which the wulfenite in the oxidized parts of lead deposits is derived is generally supposed to be molybdenite. Microscopic and chemical analyses of the galena in such deposits are desirable.

Powellite, $CaMoO_4$, is formed by the oxidation of deposits containing molybdenite. At the O K mine, in the San Francisco region, Utah,[5] it appears as yellow incrustations on quartz and some of it is pseudomorphic after molybdenite. Powellite is also found pseudomorphous after molybdenite at Rociada, N. Mex.; near Oak Springs, Nye County, Nev.; near Black Mountain, 20 miles north of Randsburg, Cal.; and at Baringer Hill, Burnet County, Tex., in pegmatite. In all these districts the powellite is clearly an alteration product of molybdenite,[5] but in the ores of the Peacock claim, Seven Devils district, Idaho, from which powellite was first described, no molybdenite is known to have been found, though Melville[6] describes an olive-green mineral accompanying the powellite which is strongly suggestive of altered molybdenite as seen in the Rinconada and other ores.[5]

[1] Curtis, J. S., Silver-lead deposits of Eureka, Nev.: U. S. Geol. Survey Mon. 7, p. 54, 1884.

[2] Crawford, R. D., A preliminary report on the geology of the Monarch mining district, Colorado: Colorado Geol. Survey Bull. 1, p. 35, 1910.

[3] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 110, 1913.

[4] Hess, F. L., Some molybdenum deposits of Maine, Utah, and California: U. S. Geol. Survey Bull. 340, pp. 239–240, 1908.

[5] Hess, F. L., written communication.

[6] Melville, W. H., Powellite (calcium molybdate), a new mineral species: U. S. Geol. Survey Bull. 90, pp. 34–37, 1892.

Molybdite, MoO_3, has been regarded as an oxidation product of molybdenite. This or a nearly related mineral very commonly occurs as fine needles incrusting molybdenite that is undergoing oxidation. Lindgren and Ransome mention a molybdenum oxide (probably molybdite) as occurring in capillary crystals in weathered phonolite of Cripple Creek, Colo.[1]

Ilsemannite, $MoO_2.4MoO_3$, is a rare oxidation product of molybdenite. In the Ophelia tunnel at Cripple Creek, Colo., according to Lindgren and Ransome,[1] a quartz vein with molybdenite, sphalerite, and pyrite has altered, forming little crusts of molybdenum oxide, probably ilsemannite, on fractured surfaces. It has been found also at Idaho Springs, Colo.[2] Ilsemannite has been noted elsewhere as a decomposition product of wulfenite.

Molybdic ocher, $Fe_2O_3.3MoO_3.7\frac{1}{2}H_2O$, has recently been identified and analyzed by W. T. Schaller.[3] He questions the existence of the simple oxide molybdite (MoO_3) as a natural mineral, and shows that a specimen which appears to be like other ochers, and which ordinarily has been called molybdite, is the hydrous ferric molybdate. Another specimen, from Nevada City, Cal.,[4] is termed a mixture of "molybdine" and iron oxide. An iron molybdate is described also from Heard County, Ga.[5] Molybdic ocher is found also in a vanadium-bearing vein near Placerville, Colo.[6]

Molybdenite, MoS_2, is not abundant but is peculiarly widespread and occurs in many associations. It is a constituent of some igneous rocks, particularly of granite and pegmatite. It occurs in both these rocks, at Catherine Hill, Maine,[7] and near Cooper, Washington County, Maine.[8] It is found in aplite dikes in the O K mine, Utah, and veins 3 or 4 inches thick are reported from pegmatitic quartz. In some specimens in this mine molybdenite fills minute fractures in chalcopyrite but is regarded as primary.[9] In the Santa Rita and Patagonia mountains, Ariz., molybdenite occurs at many places in quartz veins and as impregnations in granite. According to Schrader

[1] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 124, 1906.

[2] Laney, F. B., oral communication.

[3] Schaller, W. T., The chemical composition of molybdic ocher: Am. Jour. Sci., 4th ser., vol. 22, p. 297, 1907.

[4] Genth, F. A., Contributions to mineralogy: Am. Jour. Sci., 2d ser., vol. 28, p. 248, 1859.

[5] Taylor, W. J., Notice of a new locality of molybdate of iron: Am. Jour. Sci., 2d ser., vol. 19, p. 429, 1855.

[6] Hess, F. L., Notes on the vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, p. 151, 1913.

[7] Emmons, W. H., Some ore deposits in Maine and the Milan mine, New Hampshire: U. S. Geol. Survey Bull. 432, p. 42, 1910.

[8] Smith, G. O., Molybdenum deposits in eastern Maine: U. S. Geol. Survey Bull. 260, p. 197, 1905.

[9] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 110, 1913.

and Hill[1] the deposits are related to acidic rocks and were precipitated with quartz from thermal waters. Many deposits presumably of like origin are described by Hess.[2]

In mining camps of the southwest molybdenite is by no means rare but is nowhere abundant. At Santa Rita, N. Mex., it occurs in noteworthy quantities. It is generally more abundant in deposits as old as early Tertiary or older, but some is found also in later deposits, for example, at Cripple Creek, Colo.,[3] where molybdenite occurs as a primary mineral intergrown with pyrite and zinc blende. In that district mixed ores carry 0.04 per cent of molybdenum. Auriferous quartz veins that contain considerable molybdenum occur at Observatory Inlet, British Columbia.[4] Some specimens carry 2.6 per cent molybdenum.

In nearly all its associations molybdenite is clearly a primary mineral, though in some it is evidently of uncertain origin. Molybdenite at Monte Cristo, Wash., fills a small crack and is regarded by Spurr[5] as probably secondary. It is found also in a vanadium-bearing vein of unusual type at Placerville, Colo.[6]

TUNGSTEN.

The names and chemical composition of the principal tungsten minerals are given below:

Tungstite	WO_3.
Stolzite	$PbWO_4$.
Ferberite	$FeWO_4$.
Wolframite	$(Fe,Mn)WO_4$.
Hübnerite	$MnWO_4$.
Scheelite	$CaWO_4$.

Tungsten, like molybdenum, is a metal of the chromium group, to which belongs also uranium. Tungsten forms two oxides, the dioxide, WO_2, and the trioxide, WO_3, which is more common. Tungstic acid, H_2WO_4, is nearly insoluble. Tungsten is not a base-forming mineral, and in none of its mineral compounds does it play the part of a true metal. No silicate is known. Unlike molybdenum it does not form a sulphide.

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[1] Schrader, F. C., and Hill, J. M., Some occurrences of molybdenite in the Santa Rita and Patagonia mountains, Ariz.: U. S. Geol. Survey Bull. 430, p. 162, 1910.

[2] Hess, F. L., Molybdenum: U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 745, 1909. Also Some molybdenum deposits of Maine, Utah, and California: U. S. Geol. Survey Bull. 340, p. 231, 1908.

[3] Lindgren, Waldemar, and Ransome, F. L., op. cit., p. 120.

[4] McConnell, R. G., Observatory Inlet, British Columbia: Canada Geol. Survey Summ. Rept., p. 49, 1911.

[5] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 839, 1901.

[6] Hess, F. L., Notes on the vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, p. 151, 1913.

Potassium tungstate, K_2WO_4, is a soluble salt. In alkali solutions it does not readily hydrolyze, but in strong acid it breaks down, forming H_2WO_4. The hexachloride, WCl_6, with water, decomposes to form the trioxide, WO_3. The pentachloride, WCl_5, with water, forms a solution of the pentoxide, W_2O_5.

Ferberite, wolframite, and hübnerite are probably everywhere primary. Tungstite, or tungstic ocher, is secondary. Some scheelite is secondary. In the Black Hills botryoidal masses of scheelite 1 millimeter thick incrust wolframite. Stolzite is of uncertain origin but probably secondary.

Tungsten minerals are found in pegmatite dikes and in veins formed at all depths. Though they are very common in pegmatite and in lodes formed at considerable depth, the most productive deposits are lodes formed under moderate temperature and pressure. Of exceptional interest are the ores of the Pony district, Madison County, Mont., described by A. N. Winchell.[1] In that district schists and gneisses are cut by quartz monzonite intrusives that send off aplite and pegmatite dikes, which locally carry fluorite and pyrite. The Keystone vein, which carries precious metals and tungsten minerals, is filled near the hanging wall with pegmatite consisting of quartz, microcline, and pyrite, and near the footwall with quartz and pyrite. At a lower level the filling is chiefly pegmatite. That the precious metals and tungsten ore in this region had been deposited by ascending hot waters is indicated, according to Winchell, by its occurrence in the Boss Tweed mine below a fault that carries heavy gouge.

The iron and manganese tungstates—ferberite, wolframite, and hübnerite—form a complete series of mixtures ranging from pure iron tungstate to pure manganese tungstate.[2] The series is analogous to the plagioclase feldspar series. Hess and Schaller have identified zonal structures such as are common in the plagioclases.

The tungsten minerals in general decay or are altered very slowly by oxidation, but, as noted by Hess and Schaller,[3] under some conditions some wolframites decay readily. Specimens from Silverton, Colo.; the Eureka district, 45 miles west of Prescott, Ariz.; Cave Creek, Ariz., and some other places are extensively weathered.

Tenth-normal acids, hydrochloric or sulphuric, dissolve no determinable tungsten from scheelite, hübnerite, or wolframite in 30 days. Some scheelite goes into solution in these acids, however, if ferric salts are present.[4] Experiments in alkaline waters are not available.

[1] Winchell, A. N., The mining districts of the Dillon quadrangle, Montana, and adjacent areas: U. S. Geol. Survey Bull. 574, p. 123, 1914.

[2] Hess, F. L., and Schaller, W. T., Colorado ferberite and the wolframite series: U. S. Geol. Survey Bull. 583, p. 36, 1914.

[3] Idem, p. 8.

[4] Goldsberry, J. P., work in preparation.

Tungstates of calcium, iron, and manganese seem to be decomposed slowly by mineral waters with formation of hydrated tungstic acid, $H_2WO_4.H_2O$. This is somewhat soluble in water, and would be leached out of deposits in moist climates if exposed long enough. Tungstic acid, H_2WO_4, is less soluble in water and more stable. Pseudomorphs of pyrolusite, MnO_2, or of hematite, Fe_2O_3, after tungsten minerals, could form under conditions permitting oxidation if the ores were leached by water not more than slightly acid.

Tungstates accumulate in placers with cassiterite and other metals that are relatively stable in the oxidizing zone. Scheelite placers have been worked in the Atolia district, California,[1] ferberite placers in Boulder County, Colo.,[2] and hübnerite and wolframite placers in the Little Dragoon Mountains, Ariz.[3] Tungsten deposits that lie near the surface may be concentrated by the removal of valueless material.

Tungstite, WO_3, or probably H_2WO_4, is a common decomposition product of tungsten minerals. Under some conditions it forms pseudomorphs after tungstates. This phase of decomposition is not universal, however, and probably takes place only in acid solution. At other places iron oxides or manganese oxides occupy spaces from which iron tungstates have been dissolved, probably by alkaline waters. Ore from near Salmo, British Columbia, consisting of wolframite, scheelite, quartz, and native gold, on alteration yielded tungstic oxide. It occurs in yellow areas which contain central aggregates of minute crystals. Analyses by Walker[4] show that the material is the hydrated oxide $WO_3.H_2O$. In the Black Hills[5] tungstates, which are now mined in commercial quantities, alter on fracture planes to a golden-yellow mineral. Near Redlich, Nev., crystals of hübnerite are found in masses of quartz that are scattered over the surface, and in cavities where hübnerite has dissolved tungstite has formed.[6]

At Jardine, Mont., scheelite in the oxidized zone alters to a fibrous yellow mineral, probably tungstite.[7] Hübnerite in gold-silver veins at Butte, Mont.,[8] alters to manganese dioxide. In the Little Dragoon Mountains, Cochise County, Ariz., casts of tungsten minerals are

[1] Hess, F. L., U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 724, 1909.

[2] Hess, F. L., and Schaller, W. T., Colorado ferberite and the wolframite series: U. S. Geol. Survey Bull. 583, p. 8, 1914.

[3] Rickard, Forbes, Notes on tungsten deposits of Arizona: Eng. and Min. Jour., vol. 78, p. 263, 1904.

[4] Walker, T. L., A review of the minerals tungstite and meymacite: Am. Jour. Sci., 4th ser., vol. 25, p. 305, 1908.

[5] Irving, J. D., Economic resources of the northern Black Hills: U. S. Geol. Survey Prof. Paper 26, p. 166, 1904.

[6] Young, G. J., oral communication.

[7] Winchell, A. N., Notes on tungsten minerals from Montana: Econ. Geology, vol. 5, p. 162, 1910.

[8] Idem, p. 165.

coated with ocher.[1] Near Calabasas, Ariz., also, according to Hill,[2] wolframite alters pseudomorphously to iron oxide.

Stolzite, $PbWO_4$, the tungstate of lead, and cuproscheelite, (Ca,Cu) WO_4, are probably secondary. Cuprotungstite, a hydrous copper tungstate, occurs at Cave Creek, Ariz. It is probably secondary and accompanies ferberite and copper minerals in a pegmatite.[3]

Ferberite, $FeWO_4$, is the principal mineral of the tungsten veins of Boulder County, Colo.,[4] where small veins with quartz, calcite, adularia, chalcopyrite, and a little galena are found in granite. Precious metals, molybdenite, and tellurides are locally present. The ferberite is exceedingly resistant to weathering, and no decomposition products are noted. It forms placers that have been successfully worked. Ferberite is reported also from Gilpin County, Colo. It is found also in the Black Hills, where, on weathering, according to Hess, it leaves a skeleton of iron oxide.

Wolframite is a common ore of tungsten, and is rather widely distributed. It occurs in pegmatites and in veins formed at great depths, and also in veins formed at moderate depths. It is associated with tin in the mines of Cornwall and at many other places.

In the Black Hills wolframite is found in silicified dolomite, which it replaces.[5] Associated minerals are fluorite, pyrite, quartz, and barite. In the Black Hills wolframite, hübnerite, and ferberite are found also in quartz veins of pegmatitic origin.[6] In the Dragoon Mountains, Ariz.,[1] ores containing wolframite and associated scheelite and hübnerite replace granite. According to Rickard, scheelite is found there in seams and streaks in hübnerite, and is probably primary. The hübnerite shows well-defined zonal structure.[7] At the Trumbull mine, Trumbull, Conn., according to Hobbs,[8] ore consisting of wolframite, scheelite, and wolfram ocher occurs as a deposit 3 to 5 feet thick which lies between the contact

[1] Rickard, Forbes, Notes on tungsten deposits of Arizona: Eng. and Min. Jour., vol. 78, p. 263, 1904.

[2] Hill, J. M., Note on the occurrence of tungsten minerals near Calabasas, Ariz.: U. S. Geol. Survey Bull. 430, p. 166, 1910.

[3] Hess, F. L., written communication.

[4] George, R. D., The main tungsten area of Boulder County, Colo.: Colorado Geol. Survey Ann. Rept., 1908, pp. 7–103, 1909. Hess, F. L., and Schaller, W. T., Colorado ferberite and the wolframite series: U. S. Geol. Survey Bull. 583, p. 9, 1914. Lindgren, Waldemar, Some gold and tungsten deposits of Boulder County, Colo.: Econ. Geology, vol. 2, p. 452, 1907.

[5] Irving, J. D., Some recently exploited deposits of wolframite in the Black Hills of South Dakota: Am. Inst. Min. Eng. Trans., vol. 31, p. 683, 1901. Irving, J. D., Economic resources of the northern Black Hills: U. S. Geol. Survey Prof. Paper 26, p. 163, 1904.

[6] Hess, F. L., Tin, tungsten, and tantalum deposits of South Dakota: U. S. Geol. Survey Bull. 380, pp. 149–154, 1909.

[7] Hess, F. L., and Schaller, W. T., Colorado ferberite and the wolframite series: U. S. Geol. Survey Bull. 583, p. 30, 1914.

[8] Hobbs, W. H., The old tungsten mine at Trumbull, Conn.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 14, 1901.

of crystalline limestone and gneiss and conforms with its general dip and strike. The wolframite has replaced scheelite pseudomorphously. The process appears to begin with the development of a network of veinlets of wolframite in scheelite and ends in complete replacement. The wolframite subsequently alters to iron oxide, yielding pseudomorphs of limonite after scheelite. Many additional localities at which wolframite is found are cited by Hess and Schaller.[1]

Hübnerite, $MnWO_4$, is found at many places in small quantities but is a less valuable source of tungsten than ferberite and wolframite. Although it occurs in many pegmatites, such deposits are of little economic value. Small quantities have been mined with lode ores, particularly those of silver. These ores, however, generally contain only a little hübnerite.

According to Umpleby, hübnerite is the chief tungsten mineral at Ima, Blue Wing district, Lemhi County, Idaho.[2] It is found with fluorite in quartz veins at Pony, Madison County, Mont.[3] Notable quantities appeared in concentrations of siliceous silver ore at Combination,[4] near Philipsburg, Mont., where 20 to 1 concentrates carried one-third of 1 per cent tungsten.

Hübnerite is associated with silver ores in the Gagnon mine,[5] Butte, Mont. It has been mined also from gold-silver veins of Butte, where it is associated with quartz, pyrite, marcasite, and a little galena, sphalerite, and other minerals. On oxidation it changes finally to black oxide of manganese.[6] In New Mexico[7] it has been found in lead-silver ore in the Old Hachita district; with quartz, pyrite, and galena in the Victorio district, Luna County; and in quartz veins in the White Oaks district.

Scheelite, $CaWO_4$, like wolframite, is found in pegmatites and in veins formed in the deep zone and at moderate depths. Valuable deposits are at Atolia, San Bernardino County, Cal., in quartz calcite veins in granodiorite near a schist contact.[8] From 2 to 5 miles north-

[1] Hess, F. L., and Schaller, W. T., op. cit., pp. 26–30.

[2] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 111, 1913.

[3] Winchell, A. N., The mining districts of the Dillon quadrangle, Montana, and adjacent areas: U. S. Geol. Survey Bull. 574, p. 125, 1914.

[4] Goodale, C. W., and Akers, W. A., Concentration before amalgamation for low-grade, partially decomposed silver ores, with notes on the geology of the Flint Creek mining district: Am. Inst. Min. Eng. Trans., vol. 18, p. 248, 1890. Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 162, 1913.

[5] Pearce, R., The association of minerals in the Gagnon vein, Butte, Mont.: Am. Inst. Min. Eng. Trans., vol. 16, p. 64, 1888.

[6] Winchell, A. N., Notes on tungsten minerals from Montana: Econ. Geology, vol. 5, p. 164, 1910.

[7] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, pp. 180, 292, 336, 1910.

[8] Hess, F. L., U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 724, 1909.

west, in the Rand and Stringer districts, scheelite is found in gold veins cutting schists. In the Atolia region sands and residual surface material have been worked as dry placers. Hess and Schaller[1] state that scheelite in veins of Boulder County, Colo., commonly lines vugs and is later than ferberite, though it is not regarded as a secondary mineral. At the Trumbull mine, Connecticut, as already stated, scheelite is replaced by wolframite.

Scheelite is the principal mineral in the tungsten deposits of Jardine, Mont. It occurs in quartz veins with arsenopyrite and gold and a little pyrite and chalcopyrite. The quartz, according to A. N. Winchell[2] is smoky and contains many fluid inclusions with cubic crystals, probably of halite. A little scheelite is present in veins of quartz and a little calcite near Calabasas, Ariz.[3] In the Blue Wing district, Idaho, scheelite crusts line open spaces in quartz gangue. These, however, are primary.[4] Scheelite is associated with hübnerite in quartz veins in the Snake Range, White Pine County, Nev.[5] Near Lead, S. Dak., botryoidal masses of scheelite about 1 millimeter thick form secondary incrustations on wolframite.

URANIUM.

The names and chemical composition of the principal uranium minerals are stated below. The formulæ are chiefly those given by Hess.[6]

Carnotite.....$K_2O.2UO_3.V_2O_5.8(?)H_2O$.
Tyuyamunite.....$CaO.2UO_3.V_2O_5.8(?)H_2O$.
Torbernite.....$CuO.2UO_3.P_2O_5.8H_2O$.
Autunite.....$CaO.2UO_3.P_2O_5.8H_2O$.
Zeunerite.....$CuO.2UO_3.As_2O_5.8H_2O$.
Uranophane.....$CaO.2UO_3.2SiO_2.6H_2O$.
Uvanite.....$2UO_3.3V_2O_5.15H_2O$.
Pitchblende, an amorphous mineral containing uranium, rare earths, etc.
Gummite, hydrous uranium oxide with other bases.
Samarskite, of uncertain composition; contains uranium, iron, lime, and several rare earths.
Uraninite, a crystalline variety of pitchblende.

Uranium, like chromium, molybdenum, and tungsten, forms a trioxide. The anhydride, UO_3, with water gives H_2UO_4. There are also salts derived from diuranic acid, $H_2U_2O_7$. Besides the trioxide,

[1] Hess, F. L., and Schaller, W. T., op. cit., p. 12.
[2] Winchell, A. N., Notes on tungsten minerals from Montana: Econ. Geology, vol. 5, p. 161, 1910.
[3] Hill, J. M., op. cit., p. 166.
[4] Umpleby, J. B., op. cit., p. 79.
[5] Weeks, F. B., Tungsten deposits in the Snake Range, White Pine County, Nev.: U. S. Geol. Survey Bull. 340, p. 38, 1908.
[6] Hess, F. L., A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, vol. 9, p. 675, 1914.

UO_3, there are UO_2, U_2O_5, U_3O_8, and UO_4. The trioxide forms a soluble sulphate with sulphuric acid. Alkaline sulphide precipitates uranyl sulphide, UO_2S, which, however, is not stable. There is no native metal. In the number of its oxides and the variety of its compounds uranium rivals manganese, so that it is not surprising that there should be some difference of opinion regarding the formulæ of its compounds. With soluble sulphates and chlorides and a great variety of oxides—some acid-forming, some base-forming—the element may enter secondary compounds. Of the minerals listed above all are doubtless secondary except uraninite, samarskite, and pitchblende, and pitchblende may be in part secondary. Hess has shown[1] that gummite and uranophane form layers around uraninite from which they have altered; autunite and torbernite, being apparently more mobile, form crystals at a considerable distance from the uraninite.

Carnotite is found at Radium Hill, near Olary, South Australia,[2] in an area of metamorphic gneisses and schists cut by dikes of granite and diorite. The carnotite is found in a lode associated with quartz, biotite, magnetite, ilmenite, and rutile. It occurs as yellow powder and small platy orthorhombic crystals, coating cracks and filling cavities. With it are found chromium, vanadium, cerium, lanthanum, and yttrium, which are probably contained in the rare mineral tscheffkinite. Crook and Blake regard the gangue minerals as products of eruptive activity. They state that rutile and magnetite have resulted from breaking down of ilmenite and that the "secondary agents" introduced carnotite and minerals of the rare earths. The character of the agents is not otherwise noted.

About 1½ miles northeast of Placerville, Colo., is a vanadiferous vein which carries also a little uranium as autunite. The rocks of the district are sedimentary, lie nearly flat, and are cut by diorite porphyry intrusions and basic dikes. The deposit is in a fault fissure in the Dolores formation.[3] Near the vein the limestone wall rock is recrystallized to calcite and coated with a chromium mica. The deposit contains chalcopyrite, chalcocite, autunite, asphalt, malachite, azurite, molybdenite, molybdic ocher, and erythrite, as well as gold, silver, and vanadium. In the overlying La Plata sandstone near this vein there are valuable bedding-plane deposits. The sandstone is nearly pure quartz cemented by calcite. Certain layers carry organic matter, roscoelite, quartz, and a little pyrite, as well as carnotite, which, however, is not present in workable quantities, the ores

[1] Hess, F. L., Uranium and vanadium: U. S. Geol. Survey Mineral Resources, 1912, pt. 1, p. 1016, 1913.

[2] Crook, T., and Blake, G. S., On carnotite and an associated mineral complex from South Australia: Min. Mag., vol. 15, p. 271, 1910.

[3] Hess, F. L., Notes on the vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, p. 151, 1913.

owing their value to their content of vanadium. Near the deposits the sandstone is indurated and the calcite cement is apparently replaced by quartz. A chromium mica, probably mariposite, is deposited in the sandstone near the vanadium ore and at many places over extensive areas at the horizon of the vanadium ore. Secondary carnotite deposited in fractures has evidently been leached out of the vanadium ore. Hess regards the mariposite and roscoelite as primary.

The Placerville bedding-plane deposits were described by Ransome in 1905.[1] He considers them to have replaced calcite in the sandstone. Many of them play out when they are followed downward or into the hills by tunnels, and as they are found only near the present surface they are believed to have been formed by superficial agencies. Some of the carnotite deposits on La Sal Creek, Colo., are pockets in sandstone above a shale and some occupy fissures along planes of movement, such as might have been formed by slumping or slipping of the sandstone on the shale since the present topography was formed. Since the Placerville deposits were discovered many deposits of carnotite and other nearly related minerals have been found in the same, or approximately the same rocks, extending over a wide area in southwestern Colorado and into Utah. All the deposits appear to be in the La Plata (Jurassic) or in the McElmo (Jurassic?). Fossil wood and bones are nearly everywhere associated with the deposits, and other common associates are copper carbonates, vanadium and chromium minerals, and some pyrite. Hess mentions a deposit in the La Sal Mountains,[2] where a petrified tree was mined for ore, the uranium being richest around the edge, or the part that was probably most decayed before burial. He also states that in Bull Canyon, south of Paradox Valley, a tree trunk, between 50 and 100 feet long, was replaced by a mass very rich in carnotite, and similar occurrences are reported from Long Park, north of Paradox Valley.[3] To account for these deposits Hess proposes a hypothesis that assumes older uranium and vanadium veins in the drainage basins that supplied La Plata and McElmo sediments and cites several deposits as possible examples. Uranium and vanadium from these veins would be dissolved possibly by sulphuric acid generated by pyrite and carried to the sea, where they might be reprecipitated by decaying reeds and trees. He mentions a uranium sulphate in White Canyon, 15 miles southeast of Hite, Utah,[4] and a similar occurrence in the same region near Fruita, Wayne County.[5]

[1] Hillebrand, W. F., and Ransome, F. L., On carnotite and associated vanadiferous minerals in western Colorado: U. S. Geol. Survey Bull. 262, p. 14, 1905.

[2] Hess, F. L., A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, vol. 9, p. 681, 1914.

[3] Idem, p. 680.

[4] Idem, p. 687.

[5] Idem, p. 679.

In both places the sulphates are probably derived from oxidizing deposits of copper sulphide, and he suggests that the uranium may also have been deposited in the sandstone, possibly in combination with copper or sulphur, or both. The hypotheses of Ransome and of Hess imply solution of uranium minerals in cold mineral waters. Such an origin appears highly probable, as many of the deposits in the Colorado-Utah region are far from igneous rocks and in rocks that are not much disturbed and, as pointed out by Ransome, some are above the flat-lying shale.

In this connection the following chemical relations are noteworthy. Uranyl sulphate, UO_2SO_4, soluble and not rapidly hydrolyzed, could be easily transported. Reduction by vegetation would form readily the uranous sulphate. This uranous compound forms double compounds with alkali sulphates, such as are commonly present in beds formed under arid conditions. The compound $U(SO_4)_2.K_2SO_4.2H_2O$ is known. In the presence of air and vanadates the oxidation of such a compound could easily lead to the formation of a double uranyl potassium vanadate, such as carnotite, which would be more insoluble and precipitate out before the sulphate.

Tyuyamunite, $CaO.2UO_3.V_2O_5.8(?)H_2O$, is doubtless a secondary mineral. It has been found in the outcrops of copper veins on Red Creek, Browns Hole, in northeastern Utah, and in the oxidized zone of a pipe deposit carrying copper, vanadium, and uranium minerals in Tjua-Mujun Hill, Ferghana, Asiatic Russia.[1]

Pitchblende.—The best known deposits of uraninite, or pitchblende, are in the Erzgebirge, a mountain range between Bohemia and Saxony; in Cornwall, England; and in Gilpin County, Colo. In the Erzgebirge sedimentary and metamorphic rocks are intruded by granite, granite porphyry, and quartz porphyry. Associated with the granitic intrusions are veins of varied types of mineralization, some carrying tin, others lead and zinc, still others cobalt, nickel, and silver. At Joachimsthal, Bohemia, the pitchblende ores are associated with quartz, dolomite, pyrite, and chalcopyrite. Locally the pitchblende, quartz, and dolomite coat over the cobalt and nickel minerals. Ruby silver (proustite) occurs in veinlets cutting the pitchblende ores. At Annaberg, Saxony,[2] pitchblende in spherulitic masses coats siderite and fluorspar in the nickel-cobalt veins, which cut cassiterite veins of an earlier period. At Johanngeorgenstadt, Saxony, pitchblende coats bismuth-silver veins and incloses galena, chalcopyrite, and bismuth.

[1] Hess, F. L., A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, vol. 9, p. 676, 1914. Also U. S. Geol. Survey Mineral Resources, 1912, pt. 1, pp. 1031–1032, 1913.

[2] Müller, Hermann, Die Erzgänge des Annaberger Bergrevieres: Erläuterungen zur geol. Specialkarte des Königreichs Sachsen, p. 66, Leipzig, 1894.

In the Cornwall region, where granite batholiths intrude various sediments, there are great lodes of cassiterite and copper minerals which are cut by veins of cobalt and bismuth, with pitchblende and other minerals.[1]

At Quartz Hill, Gilpin County, Colo., pre-Cambrian schists and granites are cut by Tertiary intrusives (monzonite and bostonite porphyries). There are two types of mineralization: (1) Pyrite, quartz, tetrahedrite, rhodochrosite, and other minerals; and (2) a later type composed of quartz, calcite, galena, sphalerite, pyrite, and chalcopyrite. According to Bastin[2] pitchblende is deposited contemporaneously with pyrite and chalcopyrite. Globes of pitchblende have cores of pyrite, and are also coated with pyrite. Pitchblende also is traversed by veinlets of galena, sphalerite, and pyrite, probably of the second period of mineralization. Bastin states that the pitchblende was deposited during the earlier pyrite mineralization and that it was subsequently fractured and veined with ores of the lead-zinc mineralization. The data above appear to indicate that pitchblende is primary, although some occurrences are probably secondary.

Uraninite, the crystallized form of the mineral which in its amorphous form is known as pitchblende, is found, so far as certainly known, only in pegmatites and never in large quantities. Specimens of uraninite from northern Chihuahua, however, are in a gangue of calcite and contain visible gold. Nothing further is known of the deposit, except that some ore has been shipped for its radium content and that the mine has been worked for gold.

Uraninite is found in pegmatites in South Carolina and North Carolina, where it is largely altered to gummite, uranophane, and autunite. A few pounds are saved and sold each year as a by-product of feldspar and mica mining. It is accompanied in the dikes by samarskite and other rare minerals. It is found in pegmatites at Branchville and Glastonbury, Conn., and in the form called nivenite at Baringer Hill, Texas. It is also found in the Uluguru Mountains, German East Africa,[3] and in southern Norway.[4] The largest bodies of uraninite are found in the Singar mica mines, Gaya district, India.[5] Single pieces contain as much as 36 pounds. It is partly altered to yellow uranium ocher (uranophane?) and is accompanied by triplite. Uraninite is rather easily attacked by weathering and so is almost

[1] Pearce, Richard, Note on pitchblende in Cornwall: Cornwall Roy. Geol. Soc. Trans., vol. 9, p. 103, 1875. Penrose, R. A. F., jr., The pitchblende of Cornwall, England: Econ. Geology, vol. 10, p. 161, 1915.

[2] Bastin, E. S., Geology of the pitchblende ores of Colorado: U. S. Geol. Survey Prof. Paper 90, p. 1, 1914.

[3] Dammer and Tietze, Die nutzbaren Mineralien, vol. 1, pp. 482–483, 1913.

[4] Brögger, W. C., Die Mineralien der südnorwegischen Granitpegmatitgänge: Videnskabs-Selskabet i Christiania Skrifter, Math.-Naturv. Klasse, 1906, No. 6, Christiania, 1906.

[5] Burton, R. C., India Geol. Survey Records, vol. 44, pt. 1, pp. 24–26, 1914.

unknown in placer deposits. Dr. Vladimir Vernadsky[1] states, however, that it has been found in Siberia in gravels. Pitchblende is likewise easily altered.

Samarskite, of uncertain composition but containing uranium, iron, lime, and rare earths, is probably exclusively primary. It is not readily altered by weathering; fergusonite, which is essentially a metacolumbate and tantalate of rare earths, is much more readily altered.[2]

MANGANESE.

PRINCIPAL MANGANESE MINERALS.

The principal manganese minerals are stated below:

Pyrolusite	MnO_2.
Psilomelane	$MnO_2.2H_2O$.
Manganite	$Mn_2O_3.H_2O$.
Manganosite	MnO.
Pyrochroite	$Mn(OH)_2$.
Szmikite	$MnSO_4.H_2O$.
Mallardite	$MnSO_4.7H_2O$.
Apjohnite	$MnSO_4.Al_2(SO_4)_3.24H_2O$.
Alabandite	MnS.
Hauerite	MnS_2.
Manganostibilite	$9MnO.Sb_2O_5$.
Manganiferous calcite	$(Ca,Mn)CO_3$.
Rhodochrosite	$MnCO_3$.
Rhodonite	$MnSiO_3$.
Amethystine quartz?	
Many rock-making silicates.	

SOLUBILITIES OF MANGANESE SALTS.

At 25° C. 393 grams $MnSO_4$ will dissolve in 1,000 grams solution.[3]
At 25° C. 393 grams $MnSO_4$ will dissolve in 1,000 grams solution.[4]

OCCURRENCE AND RELATIONS OF MANGANESE MINERALS.

In the table showing the periodic classification of the elements, manganese stands on the left side of the eighth column. On the right side are its nearest neighbors, the halogens. Permanganic acid, $HMnO_4$, forms salts like perchlorates of the halogen group, but permanganates appear to play no part in weathering of ores. They are unstable in the presence of chlorine or reducing agents. I have tested manganese-bearing mine waters for permanganates, with the expected negative results. In its geologic activities manganese shows

[1] Oral communication to Frank L. Hess.
[2] Hess, F. L., written communication.
[3] Landolt-Börnstein, Physikalisch-chemische Tabellen, 4th ed., p. 481, 1912.
[4] Idem, p. 482.

very slight affiliation with the halogens. Its behavior is more like that of iron, which is its near neighbor in the ninth column of the periodic table.

The sulphate of manganese and its chloride are very soluble. Nearly all acid mine waters from pyritic manganiferous deposits carry some manganese, as manganous sulphate, $MnSO_4$, but generally only small amounts. One water from the Comstock lode, high in sulphuric acid, carries 885.1 parts manganese per million. Manganic sulphate, $Mn_2(SO_4)_3$, is formed when the oxide, Mn_3O_4, is treated with strong sulphuric acid and heated.[1] Unlike ferric sulphate, which is commonly present in mine waters, manganic sulphate, $Mn_2(SO_4)_3$, appears not to play an important part in weathering. It hydrolyzes more readily than ferric sulphate. Though possibly present, it has not been identified in mineral waters. Manganese is readily dissolved in carbonate solution, particularly with excess of carbon dioxide.

Both the sulphates and chlorides of manganese hydrolyze and form acid solutions in water. They are more stable in acid than in neutral or alkaline solution. Thus on neutralization of a manganese sulphate the oxide will be precipitated.

A series of experiments by Dr. E. C. Sullivan, made at the request of S. F. Emmons, illustrates the behavior of manganese in the course of weathering. I have abridged somewhat the statement of Dr. Sullivan.[2]

A sample of the lower white porphyry from the Thespian mine, Leadville, Colo., was finely ground and treated with carbonic acid and with sulphuric acid; the rock contained 0.8 per cent of iron and 0.033 per cent of manganese. The ratio is about 24 to 1.

Carbonic acid.—Twenty grams of the porphyry was taken in 40 cubic centimeters of water, and carbon dioxide was passed into the mixture for some hours. In 20 cubic centimeters of the solution 0.03 milligram of manganese were found and no iron. * * * To preclude the possibility that the solution of manganese was facilitated by its reduction with metallic iron introduced from the hammer in pounding up the sample, another portion was similarly treated after metallic iron and magnetite had been removed by a hand magnet. In this case 0.1 milligram of manganese and 0.02 milligram of iron were found in 20 cubic centimeters of solution.

Sulphuric acid.—Twenty grams of the powdered porphyry stood over night in contact with 40 cubic centimeters of one-tenth normal sulphuric acid (0.196 grams of H_2SO_4 in 40 cubic centimeters). This has roughly the same molecular concentration as a saturated solution of carbon dioxide. The filtrate, 20 cubic centimeters, contained 1.05 milligrams of iron, all in the ferrous condition, and 1 milligram of manganese. The experiment was repeated under the same conditions, except that contact between the rock powder and the acid was of but a

[1] Roscoe, H. E., and Schorlemmer, C., A treatise on chemistry, 4th ed., p. 1124, London, 1907.

[2] Emmons, W. H., The agency of manganese in the superficial alteration and secondary enrichment of gold deposits in the United States: Am. Inst. Min. Eng. Trans., vol. 42, p. 89, 1912.

few minutes' duration; 1.20 milligrams of iron, practically all ferrous, and 0.90 milligram of manganese were found in 20 cubic centimeters of solution.
* * *

Manganese is therefore more readily extracted from the rock than iron under surface conditions; for, although it is present in the ratio of only 1:24 as compared with iron, yet carbonic acid takes out more than three times as much manganese as iron, and sulphuric acid gives a ratio of about 1:1.

As to the precipitation of the two metals from a mixture of their salts in solution, the following experiment shows that ferrous compounds are more readily oxidized and precipitated than manganous compounds: Ferrous sulphate solution and manganous sulphate solution were mixed in equimolecular quantities (50 cubic centimeters containing 2-milligram molecules of each, i. e., 0.112 gram of iron and 0.110 gram of manganese), with sufficient powdered calcite (Iceland spar) to react with one of the metals (0.200-gram molecule of calcite). During four weeks the mixture, in a roomy flask, was occasionally shaken, the stopper at the same time being removed for a moment to allow free access of air. At the end of that time all but 1.5 milligrams of the iron had been precipitated, while the manganese was in solution in practically the same quantity as originally. Calcite, however, when in contact with manganous salts alone, in the presence of air, will precipitate the manganese as a higher oxide or hydroxide.

In the presence of oxygen and calcite or any alkaline mineral the sulphate solutions of manganese will hydrolyze and precipitate manganese oxides corresponding to limonite that is precipitated by hydrolysis of ferric sulphate. In a neutral or alkaline environment manganese oxides are as stable as those of iron, yet manganese salts may be carried in acid solutions to considerable depths before the oxides are precipitated. In a region of moderately high ground-water level I have seen seams of manganese oxide deposited in cracks of unoxidized sulphide ore about 1,000 feet below the surface. In my opinion only a little manganese is precipitated as oxide below ground-water level. (See p. 320.)

The part played by manganese in the enrichment of gold deposits has already been considered. The oxide releases nascent chlorine, which dissolves gold. Ferrous sulphate will precipitate gold, and calcite or any other alkaline mineral will precipitate both gold and manganese dioxide simultaneously.[1]

Manganese is a common element. According to Clarke[2] it forms 0.078 per cent of the average of igneous rocks analyzed, and it is present also in many sedimentary rocks, particularly in limestones and shales. It is dissolved in a strongly oxidizing environment and, like iron, is carried to the sea and precipitated as the oxide and probably also as the carbonate. The principal sources of the manganese in ore deposits are the silicates and carbonates. The sul-

[1] Emmons, W. H., op. cit., p. 28. Brokaw, A. D., The secondary precipitation of gold in ore bodies: Jour. Geology, vol. 21, p. 253, 1913. Lehner, V., On the deposition of gold in nature: Econ. Geology, vol. 9, p. 527, 1914.

[2] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 27, 1916.

phides are very rare. They are found in a few deposits, for example at Nagyag, Transylvania, at Kapnic, Hungary, and at Tombstone, Ariz. They react readily with acid solutions and decompose more rapidly than the sulphides of any other common metal. There is no native metal and no insoluble chloride. The sulphates, szmikite, mallardite, and apjohnite are so soluble that they rarely accumulate in weathered zones. The several oxides and hydroxides, pyrolusite, psilomelane, manganite, manganosite, are not deposited at depths by ascending waters but in lode deposits are everywhere secondary. The silicate rhodonite is nearly everywhere primary, and in ore bodies the carbonate is generally primary. Penrose[1] states that manganese carbonate may be deposited in bogs where organic matter is present to promote reduction, and that the carbonate is formed in veins in places where there has been no oxidation. Complex secondary carbonates, such as ankerite, that contain variable amounts of lime, iron, and magnesium, commonly carry also a little manganous oxide, without doubt as carbonate. Possibly secondary carbonate is present in the ores of Butte, Mont., and of Park City, Utah, but most lode ores contain very little secondary manganese carbonate. Manganiferous calcite is a very common gangue mineral in the western part of the United States, particularly in many gold and silver deposits formed in the middle Tertiary. On oxidation it breaks down, depositing much black manganese dioxide in the superficial zones. Ferric sulphate, as shown by Dunnington,[2] reacts very readily on manganese carbonate, forming manganese sulphate in the solution. On neutralization this breaks down and, in the presence of calcite and air, manganese dioxide is precipitated. Possibly the manganiferous solutions at depths in a neutral or alkaline environment deposit the carbonate also, although there is but little paragenetic evidence of this. In all such deposits that I have examined the carbonate appears to be primary. Although it lines vugs at some places in these deposits, it is not associated with minerals that are known to be secondary.

The manganese deposits of the United States are discussed at length by Harder.[3] Manganiferous ores are found in rocks of ages from pre-Cambrian to Recent. Nearly all of them are weathered products of manganiferous rocks and ores. Some sedimentary beds are rich enough to yield manganiferous ores by superficial concentration. On weathering, manganese oxides, like oxides of iron, tend to remain in the outcrop, and when other material is removed they

[1] Penrose, R. A. F., jr., The chemical relations of iron and manganese in sedimentary rocks: Jour. Geology, vol. 1, p. 356, 1893.

[2] Dunnington, F. P., On the formation of deposits of oxides of manganese: Am. Jour. Sci., 3d ser., vol. 34, p. 176, 1888.

[3] Harder, E. C., Manganese deposits of the United States: U. S. Geol. Survey Bull. 427, 1910.

become enriched. Some gossans and oxidized zones of fissure veins are worked for manganese. Most contact-metamorphic deposits in the western United States contain little manganese. The zinc deposits of Franklin Furnace, N. J., which have metamorphic affiliations, are, however, highly manganiferous.

In the eastern United States, on the Piedmont Plateau, the crystalline schists include manganiferous bodies here and there. According to Harder,[1] it occurs as manganous manganese in amphiboles, pyroxenes, and other minerals and by weathering is concentrated as peroxide. With it are clay, iron oxide, and silica. The manganese clearly has been dissolved and reprecipitated by ground waters, for it is concentrated in nodules or it cements rock fragments.

Some of the sedimentary rocks in the Blue Ridge west of the Piedmont area contain bedded deposits of manganese. These are superficial and are generally mixed with clay and sand. These deposits, like those in the crystalline schists, tend to segregate in nodules, but they also fill cavities and seams and replace sandstone. Paleozoic rocks in west-central Arkansas also carry manganese. Large deposits occur at Batesville,[2] where the manganese is found mainly in the Cason shale above the Polk Bayou limestone and below the Boone limestone. It is in places concentrated with clay by weathering and has accumulated on hillsides as eluvial deposits, some of them 20 feet or more thick. In the Cuyuna range, in Minnesota, great layers of manganese oxide, some of them 40 feet thick, are bedded with iron ore.

In California beds and thin bodies of manganese ores are found in jasper lenses in the Franciscan (Jurassic?) formation. Most of these beds are only a few feet thick and are not extensive laterally. At Golconda, Nev., a manganiferous bed lies between beds of calcareous tufa. This bed is remarkable in that it carries 2.2 per cent of tungsten.[3] In many lode deposits rhodonite, rhodochrosite, manganiferous calcite and siderite on oxidizing have released manganese. Iron and lime, with carbon dioxide, have been removed, with attendant concentration of manganese as oxides. Thus are formed superficial concentrations which in places are rich enough to work.

Manganese dissolved by weathering is carried to the sea and precipitated as nodules of the oxide, which are often found on the sea bottom. In bodies of fresh water bog manganese may form. At Wicks, Mont.,[4] bog manganese with iron ocher is deposited in a gulch cut in granite. Both iron and manganese oxides are found there in

[1] Harder, E. C., op. cit., p. 46.

[2] Penrose, R. A. F., jr., Manganese; its uses, ores, and deposits: Arkansas Geol. Survey Ann. Rept., 1890, vol. 1, pp. 145–147, 1891.

[3] Idem, p. 155.

[4] Harder, E. C., op. cit., p. 136.

rounded pealike masses. According to Harder, the manganese minerals have been dissolved in the weathering of granite and the metal has been precipitated nearly at the bottom of a gulch. The manganese was carried in solution at and also below the surface. It issued from the ground in springs near the bottom of the gulch.

Manganese oxides.—As stated above, the oxides of manganese are formed as the so-called "end products" of the weathering of all manganiferous minerals. Although commercially important at only a few places, these minerals are very widespread and can be found in small amounts in ores of many mining districts and as stains on igneous rocks that are undergoing oxidation. Because they are generally amorphous, it is generally impracticable to distinguish between the several oxides. In lode ores manganese oxides are found at Philipsburg[1] and at Butte,[2] Mont., where they have been formed by the alteration of rhodonite and rhodochrosite, which are commonly associated with silver ores. At Creede, Colo.,[3] thuringite on weathering has formed pyrolusite. At Norris, Mont., according to Winchell,[4] large amethyst crystals are found in pockets of loose pyrolusite near the base of the zone of oxidation, not far from the 300-foot level.

Considerable manganese dioxide has been formed from the alteration of manganiferous calcite. At Leadville, Colo.,[5] it has formed as an alteration product of manganiferous siderite. At Tombstone, Ariz., it has formed possibly in part from the sulphide. At the Delamar mine, southeastern Nevada, it appears to have been formed from the weathering of basic dikes.[6] At Ducktown, Tenn., it is formed from manganiferous garnet. Manganese oxides are present in many deposits that yield gold ores. Examples are the Annie Laurie mine, in Utah;[7] at Manhattan,[8] at Bullfrog,[9] and on the Comstock lode, Nev.;[10] at the Exposed Treasure mine, Mohave, Cal.;[11]

[1] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 156, 1913.

[2] Weed, W. H., Emmons, S. F., and Tower, G. W., U. S. Geol. Survey Geol. Atlas, Butte folio (No. 38), 1897.

[3] Emmons, W. H., and Larsen, E. S., A preliminary report on the geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. 530, p. 42, 1913.

[4] Winchell, A. N., Mining districts of the Dillon quadrangle, Montana, and adjacent areas: U. S. Geol. Survey Bull. 574, p. 115, 1914.

[5] Argall, Philip, The zinc carbonate ores of Leadville: Min. Mag., vol. 10, p. 282, 1914.

[6] Emmons, S. F., The Delamar and the Horn Silver mines: Am. Inst. Min. Eng. Trans., vol. 31, p. 658, 1901.

[7] Lindgren, Waldemar, The Annie Laurie mine, Piute County, Utah: U. S. Geol. Survey Bull. 285, p. 87, 1906.

[8] Emmons, W. H., and Garrey, G. H., Notes on the Manhattan district: U. S. Geol. Survey Bull. 303, p. 87, 1907.

[9] Ransome, F. L., Emmons, W. H., and Garrey, G. H., Geology and ore deposits of the Bullfrog district, Nev.: U. S. Geol. Survey Bull. 407, p. 94, 1910.

[10] King, Clarence, The Comstock lode, in Hague, J. D., Mining industry of the United States: U. S. Geol. Expl. 40th Par., vol. 3, p. 75, 1870.

[11] De Kalb, Courtenay, Geology of the Exposed Treasure lode, Mojave, Cal.: Am. Inst. Min. Eng. Trans., vol. 38, p. 810, 1908.

at Bodie, Cal.;[1] and near the Little Burro Mountains, in New Mexico.[2]

The weathering of wolframite or hübnerite generally releases manganese dioxide, which will incrust cavities in quartz from which the manganiferous tungstates have been dissolved. Several examples are mentioned on page 429.

Rhodonite, $MnSiO_3$, and *rhodochrosite*, $MnCO_3$, are found in lode ores of several districts in the western part of the United States. Many occurrences are mentioned above. Generally they are primary, but Weed[3] states that rhodonite at Butte, Mont., is found as concretionary masses and loose aggregates filling little seams in fault clays. At Butte also, according to Weed, the relations of rhodochrosite in places appear to indicate its formation from rhodonite. A specimen of rhodonite from Park City, Utah,[4] contained a little carbonate, possibly rhodochrosite.

At Las Cabesses, Pyrenees, France, a deposit of manganese carbonate about 164 feet wide dips with Devonian strata ("calc schists") at an angle of about 72°. According to Moreing,[5] the surface ore, which was mined for manganese oxide, passes into carbonate below. That the carbonate was valuable was discovered by the weathering to the black oxide of the supposed gangue that had been thrown on the dump.

Manganese carbonates weather much more rapidly than silicates. In the mines of Huelva, Spain, kernels of rhodonite are found in oxides high above the water level.[6]

IRON.

PRINCIPAL IRON MINERALS.

The chemical composition of the principal iron minerals is shown below.

Limonite	$2Fe_2O_3.3H_2O$.
Hematite	Fe_2O_3.
Melanterite	$FeSO_4.7H_2O$.
Jarosite	$K_2O.3Fe_2O_3.4SO_4.6H_2O$.
Siderite	$FeCO_3$.
Ankerite	$CaCO_3.(Mg,Fe,Mn)CO_3$.

[1] McLaughlin, R. P., Geology of the Bodie district, California: Min. and Sci. Press, vol. 94, p. 796, 1907.

[2] Paige, Sidney, Metalliferous ore deposits near the Burro Mountains, Grant County, N. Mex.: U. S. Geol. Survey Bull. 470, p. 132, 1911.

[3] Weed, W. H., Geology and ore deposits of the Butte district, Mont.: U. S. Geol. Survey Prof. Paper 74, p. 84, 1912.

[4] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 112, 1912.

[5] Moreing, C. A., The manganese mines of Las Cabesses, Pyrenees, France: Inst. Min. and Met. Trans., vol. 2, p. 254, London, 1894.

[6] Johnson, Frank, The manganese deposits of Huelva: Inst. Min. and Met. Trans., vol. 3, p. 275, London, 1895.

Marcasite	FeS_2.
Pyrite	FeS_2.
Pyrrhotite	Fe_7S_8.
Arsenopyrite	FeAsS.
Chalcopyrite	$FeCuS_2$.
Bornite	Cu_3FeS_4.
Magnetite	Fe_3O_4.
Greenalite	Hydrous iron silicate.
Olivine	$(Fe,Mg)_2SiO_4$.

SOLUBILITIES OF IRON SALTS.

No comprehensive table showing the solubilities of iron salts determined under uniform conditions is available to me. The solubilities of ferric and of ferrous salts differ greatly, and the experimental difficulties in determining the solubilities are considerable, owing to the changes that take place in the state of oxidation of iron. According to Atherton Seidell,[1] a liter of water at 20° C. dissolves 264.2 grams $FeSO_4.7H_2O$; a liter of water saturated with CO_2 dissolves, at 6 to 8 atmospheres, 0.73 gram $FeCO_3$; a liter of water at 15° C. dissolves 400 grams of $FeCl_2.4H_2O$ (Etard); a liter of water at 20° C. dissolves 478.8 grams $FeCl_3$. (Total $FeCl_3.12H_2O$ is 918.5 grams.)

RELATIVE ABUNDANCE OF IRON MINERALS.

Iron is abundant in nature, constituting, according to Clarke,[2] 4.18 per cent of known terrestrial matter. Its ores are formed under many geologic conditions. It is abundant in igneous rocks and in some of them it is segregated in bodies that are rich enough to mine. Some contact-metamorphic deposits and some veins of the deep zone yield iron. Some sedimentary rocks also are rich enough to mine for iron, and many rocks, both sedimentary and igneous, on weathering are converted into iron ores.

Hematite is the most important iron ore mineral. It constitutes[3] about 90 per cent of the ore mined in the United States. Magnetite and limonite supply each about 5 per cent. The other iron minerals are of interest chiefly as minerals of protores, or materials from which iron may be concentrated by weathering. Some limonite deposits are the oxidation products of iron sulphide lodes. Examples are the limonites of the Gossan lead, in Virginia, and of Ducktown, Tenn. (See p. 236.)

[1] Seidell, Atherton, Solubilities of inorganic and organic substances, New York, 1911.

[2] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 34, 1916.

[3] Harder, E. C., U. S. Geol. Survey Mineral Resources, 1908, pt. 1, p. 66.

SUPERFICIAL ALTERATION OF IRON SULPHIDE DEPOSITS.

The iron sulphides play an important part in the alteration and enrichment of deposits of the more valuable metals, and it is principally in that connection that they have been considered here.

Most mine waters contain iron, and the facility with which ferric sulphate is changed to ferrous sulphate affords the most readily available index to the state of oxidation of the solutions. The chemical processes involved in the alteration of iron sulphides, the reduction of ferric sulphate, and the removal of acid to form inert sulphates below the water level have already been discussed.

Most of the iron sulphides contain more than enough sulphur to form iron sulphate on oxidation, and the remaining sulphate may be utilized to form sulphuric acid. Ferric sulphate readily hydrolyzes, forming basic ferric sulphate and subsequently ferric hydroxide, and each step sets free sulphuric acid. The property of hydrolysis of ferric salt is important in connection with the superficial alteration and the enrichment of sulphide ores. It supplies a solvent for many of the metals; it generally results in the concentration of iron oxide at the surface, which may afford an indication that a deposit containing iron sulphide is below.

One function of basic ferric sulphate, which ultimately breaks down to form oxide, is to supply sulphate ion to solutions in the oxidized zone. Sulphates may thus be available even after all sulphides have disappeared.

As a result of the hydrolysis of ferric sulphate the larger portion of the iron is generally fixed near the surface as iron oxide. Not all is so fixed, however, for the analyses of mine waters show that iron is almost universally present in the underground circulation. It has been stated above that iron passes downward, held in sulphuric acid solution mainly as iron sulphate; that the sulphate solution reacts on sulphides and gangue minerals; and that the acidity is reduced by forming inert sulphates, chiefly those of alkalies and alkaline earths. Along with such changes in acidity ferrous sulphate is produced by reduction of ferric sulphate.

Not much ferric sulphate exists far below the water level. In air a decrease in acidity favors hydrolysis, but below the water level, where air is excluded, the decrease in acidity is attended by reduction of iron to the ferrous state. Ferrous sulphate does not hydrolyze to precipitate iron oxide. Ferrous hydrate may be formed in neutral or alkaline environment. This hydrate is light-colored but unites rapidly with free oxygen to form the brown ferric hydroxide. The mixture has a greenish appearance when distributed in a finely divided state through the precipitate.[1]

[1] Ostwald, Wilhelm, The principles of inorganic chemistry (trans. by Alex. Findlay), p. 577, London, 1904.

In little cracks in sulphide ore, at considerable depths below the highly oxidized zone, small veinlets and putty-like masses of an iron oxide that is generally assumed to be limonite are conspicuous in many deposits. Such deposits of iron oxides in the Granite-Bimetallic vein at Philipsburg, Mont., are at least 500 feet below the zone of the highly oxidized ore. Some of them doubtless have formed since the mine was opened, at places where iron sulphate solutions issued from the vein and came in contact with air. Others may be due to deposition of iron oxide or basic ferric sulphate from suspension. (See pp. 91, 100.) Possibly some are the oxidation products of ferrous sulphate or ferrous hydrate.

E. T. Allen has shown that a solution of hydrogen sulphide and ferric sulphate gives ferrous sulphate and sulphur, and in cold solutions of very low acidity ferrous sulphate with sulphur and hydrogen sulphide gives FeS_2 as pyrite and marcasite, the amount of each depending upon the acidity of the solution. It has been shown above that these conditions probably exist in the deeper zones in some deposits, but probably they exist through a comparatively narrow vertical range. In any event the precipitation of secondary iron sulphides, although known in some, is subordinate in most deposits. In nearly all lode ores pyrite is among the older minerals. Very rarely it has formed in cracks that cut other sulphides. Nevertheless we know that pyrite does form in cold solutions, for it commonly cements sandstones, and it develops in shales and other rocks far removed from evidences of igneous activity. Secondary chalcopyrite has been discussed with ores of copper (p. 195).

CONCENTRATION OF IRON BY WEATHERING OF FERRUGINOUS SEDIMENTS AND IGNEOUS ROCKS.

The concentration of iron oxides by weathering of sulphide ores has already been discussed (p. 53). More important commercially are the limonite and hematite deposits that have been formed through the weathering of ferruginous sedimentary rocks and of igneous rocks rich in iron. The iron minerals are dissolved but slowly in ground waters and where associated material is removed in solution more rapidly than iron the residual oxidized iron is concentrated. Some iron is removed in solution, however, as is shown by the presence of iron in some waters and by deposits formed from them. Different deposits behave differently. In one group residual limonite is formed; in another iron is dissolved and limonite is precipitated as a replacement of limestone; in still another group limonite remains with silica, and carbonates have been removed. In another still both carbonates and silica are eliminated, and iron oxide and a little clay remain. Why the weathering of iron-bearing

rocks is so different in different places is not thoroughly understood. In the Lake Superior districts vast quantities of silica are dissolved out, along with carbonates, but in the Appalachian region carbonates are eliminated and much silica remains. A protore containing alkalies will supply alkaline carbonates to solutions to dissolve out silica, yet some of the ores that carry very little alkali are very thoroughly leached of silica.

In the Appalachian Valley, from Vermont to Alabama,[1] there are many deposits of brown ore—limonite with some hematite. This "valley" is bordered on the east by iron-bearing crystalline rocks which have supplied iron-bearing waters for geologic ages. In the southern part of the valley, from the vicinity of Scranton, Pa., to Alabama, there has been no ice erosion and great quantities of residual material have accumulated. Such material generally has been removed from the glaciated part of the valley except from the lower parts of deposits and from those that are partly inclosed and protected by solid rock. Before the glacial epoch the country suffered long-continued weathering and many residual deposits were formed. Some also were formed as sediments. Eckel[2] mentions Tertiary fossils included in or associated with some of the beds.

The Lafayette formation was deposited over much of the southern Appalachians probably in late Tertiary time and it is of considerable importance in connection with the genesis of some of the brown ores. The bulk of the Lafayette is a reddish loam, but near its base there is a pebble bed that ranges in thickness from a few inches to several feet. Most of the pebbles are of rounded quartz and chert, but with these are associated many smooth-surfaced fragments of brown iron ore, evidently derived from near-by beds of brown ore, which must have been formed before the Lafayette formation was deposited. Where the Lafayette overlies a clay bed, so that its own basal beds have been pathways for underground waters, the iron has been gradually leached out from the upper portions of the Lafayette and redeposited as a cement around pebbles of the basal bed. Some sections show: (1) The original deposits of brown ore; (2) the derived brown-ore pebbles in the Lafayette; (3) a ferruginous conglomerate at the base of the Lafayette, consisting of siliceous pebbles and brown ore enveloped in a limonitic matrix.

A deposit near Sweetwater, Tenn., described by Burchard, illustrates the formation of residual ores by weathering. A noteworthy feature of the deposit is the development of much hematite and some manganese oxide. The deposit overlies the Chickamauga limestone, and occupies a depression on its surface. The prevailing

[1] Burchard, E. F., Butts, Charles, and Eckel, E. C., Iron ores, fuels, and fluxes of the Birmingham district, Alabama: U. S. Geol. Survey Bull. 400, 1910.

[2] Idem, p. 149.

dip of the rocks is about 15° SE. In the region southeast of Sweetwater Creek there occur, in ascending order, the Knox dolomite, Chickamauga limestone (including Holston marble lentil), and Tellico sandstone. The iron ore has evidently been derived in part from the ore beds in the Tellico sandstone and in part from the ferruginous material in the Holston marble and the rest of the Chickamauga limestone. Some beds of the Holston marble contain 15 to 20 per cent ferric oxide, and when the calcite is leached out a large iron residue is left, as is shown on the weathered edges of some beds of the marble and by fragments from which the lime has been dissolved. The deposit is residual from (1) the hematite beds in the Tellico sandstone that once extended over the area, (2) the ferric oxide in the Holston marble, and (3) the limonite streaks in other limestones of the Chickamauga. At the surface of this deposit of residual ore lumps of manganese oxide were plowed up by farmers tilling the bright-red soil. Pits were afterward sunk in search of manganese ores and they encountered workable iron ore. One pit, about 20 feet deep, showed from the top downward residual soil, sandy red clay, smooth fine-grained dark bluish-red clay, manganese oxide gravel, lumps of red iron oxide, black banded clay, and at the bottom ferruginous limestone dipping 8° to 10°. The manganese ore carried 43 to 46 per cent metallic manganese and a little iron.

The Clinton ores,[1] which are extensively developed in the eastern part of the United States, are principally hematite. They occur as lenses in sandstone and shale, and some are as much as 40 feet thick and extensive along the strike. The rocks have been folded and deeply eroded. Two types of ores are noteworthy—the fossil ore, made up of fragments of fossils, and the oolitic ore, made up of small spherules. In its unaltered state the ore is "hard," but near the surface, where it is weathered, it has become "soft" and porous. These ores are believed to be of marine origin, the iron having replaced the calcium carbonate before the ores were deeply buried. The ores were formed, therefore, before the beds were tilted, and the primary ore bears no relation to the present surface.[2]

As stated by Burchard,[3] the Clinton ores below water level generally carry much calcium carbonate and less amounts of magnesium carbonate. When the ore is exposed to the action of waters charged with carbon dioxide the calcium and magnesium carbonates are dissolved and carried off in solution by the water. The other chief

[1] Burchard, E. F., The red iron ores of east Tennessee: Tennessee Geol. Survey Bull. 16, p. 54, 1913.

[2] Smyth, C. H., jr., On the Clinton iron ores: Am. Jour. Sci., 3d ser., vol. 43, p. 487, 1892. Burchard, E. F., Butts, Charles, and Eckel, E. C., Iron ores, fuels, and fluxes of the Birmingham district, Alabama: U. S. Geol. Survey Bull. 400, p. 28, 1910.

[3] Burchard, E. F., Butts, Charles, and Eckel, E. C., op. cit., p. 35.

constituents of the ore—iron oxide, silica, and alumina—are little affected by the water.

Analyses showing effect of leaching in Clinton ores.[a]

	Fossil ore.		Oolitic ore.	
	Original (hard) ore.	Leached (soft) ore.	Original (hard) ore.	Leached (soft) ore.
Silica (SiO_2)	8.71	18.64	16.82	23.04
Alumina (Al_2O_3)	3.67	7.85	3.54	4.85
Iron oxide (Fe_2O_3)	30.24	64.71	46.04	63.07
Lime (CaO)	20.64	.....	9.96	.....
Magnesia (MgO)	7.84	.....	3.41	.....
Carbon dioxide (CO_2)	24.78	.....	13.62	.....

[a] Burchard, E. F., Butts, Charles, and Eckel, E. C., op. cit., p. 37.

A series of analyses of ores from Chamberlain, Tenn.,[1] also shows a loss of lime carbonate with other subordinate changes.

Analyses and specific gravity tests of hard, semihard, and soft "Rockwood" iron ore from Chamberlain, Tenn.

	1	2	3	4
SiO_2	5.00	7.92	7.63	7.62
Al_2O_3	2.82	3.07	3.64	4.31
Fe_2O_3	36.44	50.60	67.60	74.96
FeO	2.20	2.44	4.47	.10
MgO	1.63	1.71	.50	.47
CaO	24.84	13.77	1.68	.40
Na_2O	.10	.10	.12	.13
K_2O	.22	.25	.33	.30
TiO_2	.11	.10	.26	.12
CO_2	19.89	12.29	3.04	.32
P_2O_5	.99	1.31	1.69	1.22
S	.05	.05	.07	.02
Mn	.30	.33	.58	.31
H_2O-	.89	.59	.84	.66
H_2O+	4.72	5.52	8.15	9.35
	100.20	100.05	100.29	100.60
Fe (from Fe_2O_3 and FeO)	27.22	37.32	52.55	50.79
Specific gravity	3.05	3.09	2.49	2.59

1. Hard ore, large lump, remote from line of division between hard and soft ore.
2. Semihard, small slab, near line of division between hard and soft ore.
3. Soft, small slab, near line of division between hard and soft ore.
4. Soft ore, large lump, remote from line of division between hard and soft ore.

The Mesabi[2] iron ores are superficial concentrations in the Biwabik formation of the upper Huronian (Algonkian). The Biwabik, or iron-bearing formation, as stated by Leith, is about 800 feet thick and extends along the Mesabi range for about 100 miles. It dips

[1] Burchard, E. F., The red iron ores of East Tennessee: Tennessee Geol. Survey Bull. 16, p. 76, 1913.

[2] Winchell, N. H. and H. V., Minnesota Geol. and Nat. Hist. Survey Final Rept., vol. 5, p. 990, 1900. Spurr, J. E., The iron-bearing rocks of the Mesabi range in Minnesota: Minnesota Geol. and Nat. Hist. Survey Bull. 10, 1894. Leith, C. K., The Mesabi iron-bearing district of Minnesota: U. S. Geol. Survey Mon. 42, 1904.

from 5° to 20° nearly everywhere southeastward, and owing to its low dip forms a belt from one-fourth mile to 3 miles wide. The iron ores are covered with glacial drift, which is from 20 to 200 feet thick. The workable ore rarely extends to depths of more than 400 feet below the drift but is at some places thicker. These bodies of rich ore cover extensive areas. The unweathered Biwabik formation is composed of ferruginous chert, greenalite (ferrous silicate), ferruginous slate, and other rocks. As stated by Spurr, such material is by oxidation converted into taconite; by oxidation and removal of silica into high-grade ore. The processes have been studied and their results worked out quantitatively by Van Hise, Leith, and Mead.[1]

In the Stevenson mine four samples were taken from a layer in which the ore grades into taconite. No. 1 is fresh or but slightly altered protore; No. 4 is the leached or low-grade iron ore; and Nos. 2 and 3 are intermediate, partly altered. The chemical analyses and the volume composition are given in the table below:

Analyses of ferruginous material of the Mesabi range in various stages of alteration.

	1	2	3	4
Chemical composition:				
Fe	29.47	33.01	35.26	48.88
SiO_2	52.89	50.06	43.44	25.03
P	.016	.016	.013	.015
Al_2O_3	.62	.35	.40	.21
Loss on ignition	2.92	1.65	4.48	3.83
Volume composition:				
Pore space	8.00	16.50	26.30	52.70
Hematite and limonite	32.35	31.25	33.51	30.81
Quartz	57.90	51.40	39.30	16.18
Kaolin	1.74	.93	.92	.34

The greenalite alters to taconite or to ferruginous chert, which in turn alters to iron ore by the loss of silica. Through the leaching process magnesia, small amounts of lime, and alkalies are also dissolved out, and these aid in the solution of silica. The net result is to concentrate the iron and to develop corresponding pore space, which, however, is decreased by the slumping of the cellular, porous, weak iron ore. Evidence of such slumping is found in many of the mines, where the ore beds dip toward the thicker and richer parts of the ore body, which in general are near the central portions.

Concentration of this nature in places where water solutions have found more ready access has been going on through long geologic periods. That it was well advanced in Cretaceous times is shown in the detrital ore of the Cretaceous, which carries abundant iron ore in the form of polished pebbles.

[1] Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 194, 1911.

In the Penokee-Gogebic range of Wisconsin[1] and Michigan the rocks correspond in a broad way to those of the Mesabi. The iron-bearing rocks are the Ironwood formation of the upper Huronian, of similar age to the Biwabik. It strikes about N. 30° E. and is well defined for a distance of 80 miles. It rests on quartzite and is overlain by shale. It dips northwest at high angles, so that the outcrop is rarely more than 1,000 feet wide. It is cut by numerous basic dikes, which form pitching troughs with a quartzite footwall, and down these troughs there appears to have been a vigorous circulation of water.

The Ironwood consists chiefly of cherty iron carbonate, ferruginous slate, and subordinate greenalite. By weathering these rocks are converted into rich iron ore, mainly hematite. In the Newport mine weathering is thorough more than 2,400 feet vertically below the surface. In figure 29 the changes due to weathering and concentration are shown diagrammatically.

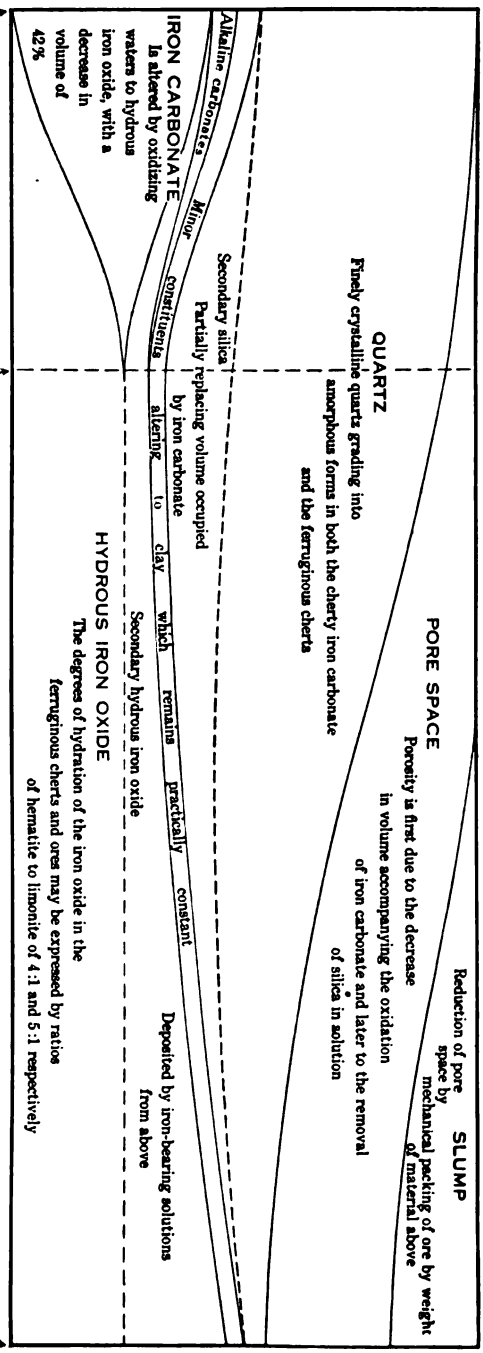
Average cherty iron carbonate
Average ferruginous chert
Average ore
IRON CARBONATE
Is altered by oxidizing waters to hydrous iron oxide, with a decrease in volume of 42%
Alkaline carbonates
Minor constituents
Secondary silica
Partially replacing volume occupied by iron carbonate
QUARTZ
Finely crystalline quartz grading into amorphous forms in both the cherty iron carbonate and the ferruginous cherts
PORE SPACE
Porosity is first due to the decrease in volume accompanying the oxidation of iron carbonate and later to the removal of silica in solution
SLUMP
Reduction of pore space by mechanical packing of ore by weight of material above
altering to clay which remains practically constant
Secondary hydrous iron oxide
Deposited by iron-bearing solutions from above
HYDROUS IRON OXIDE
The degrees of hydration of the iron oxide in the ferruginous cherts and ores may be expressed by ratios of hematite to limonite of 4:1 and 5:1 respectively

FIGURE 29.—Diagrammatic representation of changes involved in alteration of cherty iron carbonate to ferruginous chert and ore in the Gogebic district. After Van Hise, Leith, and Mead.

[1] Van Hise, C. R., and Leith, C. K., The geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 225, 1911.

OCCURRENCE OF IRON MINERALS.

Limonite, $2Fe_2O_3.3H_2O$, is generally the most abundant of the iron oxides of the altered zones, which are mainly but not altogether hydrated oxides. It is precipitated from solution and commonly occurs as a pseudomorphous replacement of pyrite and other iron minerals. As shown in the equations stated on page 106, pyrite is converted in the vadose zone to ferrous sulphate. Since oxygen is present in excess, the ferrous salt is converted to ferric sulphate, which in turn hydrolyzes to ferric hydrate.

$$6FeSO_4+3O+3H_2O=2Fe_2(SO_4)_3+2Fe(OH)_3.$$
$$4Fe(OH)_3=2Fe_2O_3.3H_2O+3H_2O.$$

These reactions indicate merely certain steps in the processes. An intermediate step may involve the precipitation of basic ferric sulphate.

The several hydrated iron oxides are:

		Ratio of Fe_2O_3 to H_2O.
Turgite	$2Fe_2O_3.H_2O$	2 to 1
Goethite	$Fe_2O_3.H_2O$	2 to 2
Limonite	$2Fe_2O_3.3H_2O$	2 to 3
Xanthosiderite	$Fe_2O_3.2H_2O$	2 to 4
Limnite	$Fe_2O_3.3H_2O$	2 to 6

Ferric hydrate, $Fe(OH)_3$, corresponds to limnite, but through processes of drying or with scant supplies of water the oxides which are less highly hydrated will form. Thus limonite forms from limnite and turgite forms when limonite is dehydrated. Turgite, which contains some combined water, but less than limonite, is probably more common in gossans than is generally supposed. The hydrated iron oxides are probably not deposited by ascending hot waters except near the orifices of hot springs.

Very commonly limonite forms, replacing carbonates of lime, iron, zinc, and other metals. Pseudomorphs after siderite, monheimite, and sphalerite are common. Pseudomorphs of limonite after cerusite are found in the Bunker Hill mine, Burke, Idaho.[1] Limonite is very commonly pseudomorphous after pyrite and chalcopyrite. When ores containing iron sulphides are oxidized much hydrous iron oxide is precipitated from solution, and stalactites, stalagmites, and grape-like masses are commonly developed. Limonite forms hollow iron straws in the Mary mine, at Ducktown, Tenn., where iron sulphate on surfaces of droplets is oxidized as it drips from the roof in shallow workings. Limonite stalactites form on the 900-foot level of Silver

[1] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 18, 1910.

Bow mine, Butte, Mont.[1] At Bingham Canyon, Utah, along the creek beds, according to Rogers,[2] hollow plant stems are replaced by limonite.

The common occurrence in mining districts of conglomerate or gravel cemented by iron oxide precipitated from waters issuing from sulphide deposits that are undergoing oxidation has already been mentioned. Limonite is the common product of the weathering of all ferruginous rocks and ores. The residual limonite from serpentines and other rocks form valuable ore bodies, as above noted.

Jarosite, $K_2O.3Fe_2O_3.4SO_3.6H_2O$, is a brownish-yellow basic sulphate that resembles some limonite in color and is commonly mistaken for limonite. It is micaceous in form and sticks to the fingers like fine flakes of graphite. It is a common oxidation product of iron sulphide, particularly in arid and semiarid countries. It has been identified in the Tintic[3] district, where it occurs as druses, nodules, and incrustations. It is known at Mercur[4] and in the Marysvale district,[5] Utah, and in the San Francisco and near-by districts, according to Butler, it is common. It was found at the outcrop of the Amethyst vein, at Creede, Colo. Small crystals associated with kaolin and limonite were identified at the Brown Palace mine, Rosebud, Nev.[6] In deposits near Tyrone, N. Mex.,[7] jarosite is found with quartz and probably also with kaolin in cracks cutting turquoise and other alteration products. Knopf[8] has described jarosite veinlets in the Yellow Pine district, Nevada, that carry much gold and platinum.

Melanterite and other sulphates and basic sulphates form abundantly in the oxidized zones[9] of some deposits of sulphide ores. The sulphates are highly soluble and are therefore unstable. In some mines they are conspicuously developed, however, on mine timbers and on the faces of ore and wall rock. Weed states that ferrous sulphate is carried by moisture of the air circulating in mine workings.[10] Jarosite and other basic sulphates are much less soluble than

[1] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 82, 1912.

[2] Rogers, A. F., op. cit., p. 21.

[3] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 702, 1899.

[4] Spurr, J. E., Economic geology of the Mercur mining district, Utah: U. S. Geol. Survey Sixteenth Ann Rept., pt. 2, p. 440, 1895.

[5] Butler, B. S., Occurrence of complex and little known sulphates and sulpharsenates as ore minerals in Utah: Econ. Geology, vol. 8, p. 320, 1913.

[6] Ransome, F. L., Reconnaissance of some mining districts of Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 67, 1910.

[7] Paige, Sidney, On the origin of turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 7, p. 382, 1912.

[8] Knopf, Adolph, A gold-platinum-palladium lode in southern Nevada: U. S. Geol. Survey Bull. 620, p. 7, 1915.

[9] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, 1913.

[10] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 99, 1912.

the sulphates and persist in some lodes even at the outcrops. The basic sulphates, as already stated, are formed as intermediate products in the hydrolysis of ferric sulphate to form ferric hydroxide. Many examples are known. Rogers[1] mentions an interesting occurrence 5 miles northwest of San Jose, Cal. Between central pyrite crystals and limonite a basic ferric sulphate, probably copiapite, is developed. Such relations and the abundance of limonite in the gossans indicate that the basic sulphates ultimately lose the sulphate radicle to form hydroxides. By these processes, doubtless, the downward migration of some of the sulphuric acid is delayed and sulphuric acid is contributed to the solutions that percolate through the oxidized ore even after all the iron sulphides have been altered.

Siderite and ankerite.—Siderite is rare as a constituent of contact-metamorphic deposits, but it is found in several veins of the deep zone and also in the gangue or in the altered wall rock of deposits formed at moderate depths by hot ascending water. High temperatures are not necessary for its genesis, however, for it is most abundant in cherty iron carbonate ores of sedimentary origin. In lode ores siderite is in the main primary. Noteworthy examples are the silver-lead veins of the Wood River[2] and Coeur d'Alene[3] districts, Idaho. It is found less abundantly also in altered wall rock at Tonopah, Nev.,[4] at Breckenridge, Colo.,[5] and in many other districts.

As a secondary mineral siderite is not abundant. Ferrous carbonate dissolves readily in acids,[6] and it could not form in a highly acid environment. At the greater depths, where the environment is alkaline or basic, ferrous carbonate could be precipitated. Siderite is present in fractures in ore of the Highland Boy mine, Bingham, Utah,[7] and according to Ransome ferrous carbonate is deposited in veinlets crossing the sulphide ore of Breckenridge.[8] In some of its occurrences ferrous carbonate has been precipitated as ankerite, a salt that also contains, in isomorphous combination, lime carbonate, manganese carbonate, and magnesium carbonate. These salts are somewhat soluble in acid, but none are highly soluble in water.

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[1] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 21, 1910.

[2] Lindgren, Waldemar, The gold and silver veins of Silver City, De Lamar, and other mining districts in Idaho: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 190, 1900.

[3] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, pp. 95–97, 1908.

[4] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 248, 1905.

[5] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 87, 1911.

[6] Ostwald, Wilhelm, The principles of inorganic chemistry (trans. by Alex. Findlay), p. 580, London, 1904.

[7] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, p. 116, 1905.

[8] Ransome, F. L., op. cit., p. 169.

Marcasite is rare or unknown as a primary mineral of igneous rocks, of pegmatites, of contact-metamorphic deposits, and of veins of the deep zones.

It is rarely formed at moderate depths by hot ascending waters but has been formed near the surface and at the orifices of hot springs. It is abundant in the lead and zinc deposits of the Mississippi Valley, where it appears to have been formed by cold solutions near the surface. As pointed out by Allen,[1] it is to be regarded as a low-temperature mineral deposited in acid solutions. In some pyritic veins it has formed as a secondary sulphide. It may be formed artificially by treating ferric sulphate with hydrogen sulphide. If the solution contains as much as 1 per cent of free sulphuric acid and the temperature is not above 100°, the product is all marcasite. At higher temperatures or in more feebly acid solutions pyrite will form.

At Ducktown, Tenn., marcasite is found sparingly in cracks associated with manganese dioxide about 200 feet below the chalcocite zone. At Goldfield, Nev., according to Ransome,[2] marcasite is rather characteristic of soft, crushed ore and of gouge and appears in many places to be of later origin than most of the other sulphides. It is a constituent of most of the high-grade ore and in much of it is as old as gold, goldfieldite, etc. It occurs as concentric, radially fibrous shells in soft, dark, and probably enriched ore streaks. As a rule these shells disintegrate on exposure to the air, with the formation of yellow films, apparently containing a little free sulphur, and of a brown fibrous efflorescence of iron sulphate. It is also a fairly abundant constituent of the rich primary ore, associated with gold, pyrite, goldfieldite, alunite, quartz, etc.

At Sudbury, according to Coleman,[3] marcasite occurs in a number of the mines, largely replacing pyrrhotite. In the Murray mine crystals were found in veins crossing pyrrhotite ore. Some of the massive marcasite carries as much as 4.5 per cent nickel, which is believed to be developed in place of iron.

Pyrite is formed under varying conditions of temperature and from solutions of many kinds. It is one of the group termed by Lindgren "persistent" minerals. It is much more abundant, however, in ores associated with igneous activities than in deposits formed by cold solutions or in secondary deposits, where, however, it is not unknown. At Steamboat Springs, Nev., Lindgren found pyrite in deposits formed in gravel by hot waters at depths not greater than 30 feet.[4] Pyrite is contained in some coal beds and is common in

[1] Allen, E. T., Sulphides of iron and their genesis: Min. and Sci. Press, vol. 103, p. 413, 1911.

[2] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 115, 1909.

[3] Coleman, A. P., The Sudbury nickel deposits: Ontario Bur. Mines Rept., 1908, pp. 235–299; The nickel industry, with special reference to the Sudbury region, Ontario, p. 22, Canada Dept. Mines, Mines Branch, 1913.

[4] Lindgren, Waldemar, The occurrence of stibnite at Steamboat Springs, Nev.: Am. Inst. Min. Eng. Trans., vol. 36, p. 27, 1906.

sedimentary rocks remote from igneous intrusives. Iron sulphide is not deposited in highly acid waters but may be deposited in slightly acid or in neutral solutions.

Pyrite as well as marcasite may be obtained by the action of hydrogen sulphide on ferric sulphate solution. Hydrogen sulphide reduces ferric sulphate to ferrous sulphate, with the separation of sulphur, and further action of hydrogen sulphide on ferrous sulphate slowly gives FeS_2. The reaction is—

$$FeSO_4+H_2S+S=FeS_2+H_2SO_4.$$

This reaction goes on, even at ordinary temperatures, in solutions that contain less than 1 per cent of free sulphuric acid. In solutions of greater acidity and at lower temperatures marcasite will form.[1]

Boss states[2] that the sulphide FeS_2 as first precipitated is a colloid (melnikovite) and that it changes gradually to the stable form, pyrite.

A. R. Whitman[3] obtained pyrite crystals in the cold from solutions that had been heated for long periods at low temperatures. A dilute solution of sulphuric acid and ferrous sulphate was passed slowly through a system of tubes containing crushed andesite, pyrite, and chalcopyrite, and heated to 45°. The solution passed about a drop a minute for five months from these tubes to a tube containing andesite, asphalt, charcoal, and iron. From this tube it was conducted to one containing kaolin and pyrite, where new pyrite cubes, the largest 1 millimeter in diameter, were formed. In another experiment dilute acid potassium carbonate solution was passed through a box containing tubes filled with crushed andesite, pyrite, and chalcopyrite, heated to 45° C. From these tubes it entered a cold tube containing chlorite, olivine, and magnetite, and thence to a tube containing kaolin, also cold. After five months pyrite had formed, but not so much as from the solution containing sulphuric acid and ferrous sulphate. In the experiment with sulphuric acid and ferrous sulphate the acid solution dissolved iron at 45° and became alkaline doubtless through the attack of acid on andesite, for aluminum sulphate was detected by analyses of the solutions. The chalcopyrite appears to have been but little affected. Incidentally this experiment shows again the insolubility of copper sulphide in alkaline solutions or the greater stability in alkaline solutions of copper minerals compared with iron minerals.

At the surface and above ground water pyrite oxidizes to basic sulphates and to limonite, but it alters in the presence of oxygen more

[1] Allen, E. T., Crenshaw, J. L., and Johnston, John, the mineral sulphides of iron, with crystallographic study by E. S. Larsen: Am. Jour. Sci., 4th ser., vol. 33, p. 169, 1912.

[2] Boss, Bruno, Melnikowit, ein neues Eisenbisulfid, und seine Bedeutung für die Genesis der Kieslagerstätten: Zeitschr. prakt. Geologie, vol. 20, pp. 453–483, 1912.

[3] Whitman, A. R., The vadose synthesis of pyrite: Econ. Geology, vol. 8, p. 455, 1913.

slowly than marcasite or pyrrhotite. In some deposits it persists to the very surface, and, unoxidized, it is found in placer deposits, especially in northern, recently glaciated areas.[1] Its occurrence in placers is not limited to these areas, for it is found in auriferous gravels in California,[2] Colorado, and other Western States.

Geikie[3] states that fresh crystals of pyrite may be seen projecting from slates that have been exposed to the atmosphere for several generations.

Examples of secondary pyrite are rare, but some have been reported.

According to Spurr, Garrey, and Ball,[4] pyrite is secondary in the Georgetown region, Colorado, where it has probably been deposited by descending surface waters. Hintze states that pyrite is pseudomorphous after silver glance at Joachimsthal. Veinlets of pyrite cut pyrrhotite copper ore at Ducktown, Tenn., and appear to have been deposited by descending waters. At De Lamar, Idaho, secondary pyrite is associated with kaolin.[5]

Secondary pyrite is found in cracks in amphibolitic schist in the F. M. D. mine, near Evergreen, Jefferson County, Colo.[6] In view of the widespread distribution of iron, however, it is remarkable that so few occurrences of secondary pyrite have been reported from the sulphide deposits in the western United States. At Ducktown, Tenn., and in some other copper districts, pyrite crystals of idiomorphic character are surrounded by pyrrhotite and other minerals. In this district the crystallization of much of the pyrite appears to have preceded somewhat that of other primary minerals. Pyrite coats enargite in ore from Morococha, Peru, and in ores from the Wild Cat mine, Santa Rita, N. Mex.[7]

Pyrrhotite, so far as is indicated by its geologic relations, is distinctly a high-temperature mineral. This conclusion is supported also by the recent synthetical work done by Allen, Crenshaw, Johnston, and Larsen,[8] who found that pyrrhotite is formed by the decomposition of pyrite in hydrogen sulphide at high temperatures.

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[1] Brooks, A. H., A reconnaissance of the Cape Nome and adjacent gold fields of Seward Peninsula, Alaska, in 1900, U. S. Geol. Survey special pub., 1901.

[2] Becker, G. F., Some features of the Rand Banket: Econ. Geology, vol. 4, p. 379, 1909.

[3] Geikie, Archibald, Textbook of geology, 4th ed., p. 108, 1903.

[4] Spurr, J. E., Garrey, G. H., and Ball, S. H., Economic geology of the Georgetown quadrangle, Colorado: U. S. Geol. Survey Prof. Paper 63, p. 144, 1908.

[5] Lindgren, Waldemar, The gold and silver veins of Silver City, De Lamar, and other mining districts in Idaho: U. S. Geol. Survey Twentieth Ann. Rept., pt. 3, p. 124, 1900.

[6] Lindgren, Waldemar, Copper in Chaffee, Fremont, and Jefferson counties, Colo.: U. S. Geol. Survey Bull. 340, p. 15, 1908.

[7] Graton, L. C., and Murdoch, Joseph, The sulphide ores of copper; some results of microscopic study: Am. Inst. Min. Eng. Trans., vol. 45, p. 40, 1914.

[8] Allen, E. T., op. cit., p. 414. Allen, E. T., Crenshaw, J. L., and Johnston, John, p. 169.

Pyrrhotite is a primary constituent of igneous rocks[1] and commonly occurs in magmatic segregations,[2] in pegmatite veins, in contact-metamorphic deposits, and in veins formed in the deeper zones. A number of its occurrences are mentioned on page 152. Pyrrhotite appears to be confined to the deeper levels in the Coeur d'Alene district,[3] Idaho, and was noted in white marble on deep levels of the Elkhorn mine, Montana.[4] In the Homestake mine, Black Hills, S. Dak., pyrrhotite is abundant in gold ores of deep levels but comparatively rare near the surface, where pyrite is the predominating iron sulphide.[5] Pyrrhotite occurs also in deposits in the Monte Cristo district, Washington,[6] and in many deposits of copper ores.

In the Sudbury nickel ores pyrrhotite appears to be somewhat older than chalcopyrite. Much of the pyrrhotite at Ducktown is older than chalcopyrite, but it is in part contemporaneous with chalcopyrite and sphalerite. As a secondary sulphide deposited by descending solutions pyrrhotite is unknown. Winslow[7] mentions the occurrence of pyrrhotite in the disseminated lead ores of southeastern Missouri, but Buckley[8] does not list it with the ore minerals of this district.

Magnetite, Fe_3O_4, is a common constituent of igneous rocks and of magmatic segregations.[9] It is present in some pegmatites, in most contact-metamorphic deposits, in vein deposits of the deeper zones, and in some ore bodies that are transitional in character between the deposits of the deep zone and those formed at moderate depth. It very rarely occurs in fissure fillings in ore bodies formed at moderate depth, but at some places it occurs in greatly altered wall rock near such filled fissures. Where the alteration is less intense, usually at some distance from the ore, small dots of magnetite form as a result of alteration of the ferromagnesian minerals by the spent ascending ore-depositing thermal solutions.

The solution tension of magnetite is very low. It oxidizes less readily than pyrite, but it will ultimately break down. In the

[1] Bastin, E. S., A pyrrhotitic peridotite from Knox County, Maine: Jour. Geology, vol. 16, p. 124, 1908.

[2] Coleman, A. P., The Sudbury nickel deposits: Ontario Bur. Mines Rept., 1903, p. 277.

[3] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, pp. 92, 130, 1908.

[4] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Mont.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 467, 1901.

[5] Sharwood, W. J., oral communication.

[6] Spurr, J. E., The ore deposits of Monte Cristo, Wash.: U. S. Geol. Survey Twenty-second Ann. Rept., pt. 2, p. 803, 1901.

[7] Winslow, Arthur, The disseminated lead ores of southeastern Missouri: U. S. Geol. Survey Bull. 132, p. 28, 1896.

[8] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties, Mo.: Missouri Bur. Geology and Mines, vol. 9, pt. 1, 1909.

[9] Hastings, J. B., Association of magnetite with sulphides in mineral deposits: Min. and Sci. Press, vol. 97, pp. 333, 358, 1908.

Philipsburg quadrangle, Montana, where sulphide ores are strongly weathered, magnetite ores similarly exposed are only slightly oxidized, and outcrops of magnetic iron are relatively more common than outcrops of pyrite, which is the most stable iron sulphide under oxidizing conditions. Where it is primary, magnetite may be a residual mineral in the oxidized zone of any deposit. Minute dark magnetite particles, few if any of them showing crystal form, are found also in the outcrops of many deposits formed at moderate depth, in which the primary ore is free from magnetite. Their minute size and possibly their lack of crystal form will usually serve to distinguish these particles from particles of primary magnetite.

The extent to which magnetite may form in the outcrop of a sulphide ore body is a matter of considerable importance in connection with the prospecting of gossans, and it has been suggested that it forms in considerable quantities near the surface as a result of certain peculiar climatic conditions.[1] Many outcrops of magnetite have been regarded as the cappings of sulphide ore bodies and have been followed downward in the hope of finding sulphide ores of gold, silver, or copper. At most places it has been found that massive magnetite is of primary origin and is persistent in depth. If rock-making minerals or the heavy silicates, such as garnet, actinolite, chlorite, and dark mica, are intergrown with the masses of magnetite, it may safely be regarded as a primary deposit and not a product of oxidation.

NICKEL.

PRINCIPAL NICKEL MINERALS.

The principal nickel minerals are given below:

Native nickel	Ni.
Morenosite	$NiSO_4.7H_2O$.
Bunsenite	NiO.
Zaratite	$NiCO_3.2Ni(OH)_2.4H_2O$.
Garnierite	$H_2(Ni,Mg)SiO_4$+aq.
Genthite	$2NiO.2MgO.3SiO_2.6H_2O$.
Annabergite	$Ni_3As_2O_8.8H_2O$.
Millerite	NiS.
Niccolite	NiAs.
Chloanthite	$NiAs_2$.
Gersdorffite	NiAsS.
Polydymite	Ni_3FeS_5.
Pentlandite	(Fe,Ni)S.

[1] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 106, 1910.

SOLUBILITIES OF SALTS OF NICKEL.

The solubilities of nickel salts in water are shown below. The number in each square shows the number of grams of the anhydrous salt held in a liter of solution:

$NiSO_4$.[a]	$NiCl_2$.[b]
274.8	391

[a] At 22.6° C., Steele and Johnson. See Seidell, Atherton, op. cit., p. 40.
[b] At 20°.

NATURE AND RELATIONS OF NICKEL MINERALS.

Nickel is not uncommon in igneous rocks and constitutes, according to F. W. Clarke,[1] an average of 0.02 per cent of them. It is generally found in basic igneous rocks, particularly in those that contain much olivine.

Nickel is closely allied to iron on the one hand and to cobalt on the other. It is both bivalent and trivalent. The nickelous and nickelic oxides correspond to similar oxides of iron. Nickelic salts do not form so readily as ferric salts, and unlike ferrous salts nickelous salts are not oxidized by air to nickelic salts. There are few compounds in which nickel is trivalent. The oxides Ni_2O_3 and $Ni(OH)_3$ are known in the laboratory but are unstable in ore deposits. Ferric salts, according to Stokes,[2] readily attack nickel compounds. Both the chloride and sulphate are soluble. From soluble solutions, according to Schuermann, the sulphide is precipitated by sulphides of cobalt and iron. Because its sulphate is so soluble nickel is readily removed from its deposits. Because nickel sulphate does not oxidize and hydrolyze like iron to form the trivalent oxide, iron and nickel in sulphide ores will separate by weathering, much of the iron remaining behind in the gossan while the nickel is carried away in solution. The gossan of nickeliferous pyrrhotite deposits is essentially limonite.

If arsenic is present nickel forms with it a moderately stable salt, annabergite, or "nickel bloom," which is frequently found at the very surface and may indicate the presence of a nickeliferous deposit below. Hydrous nickel magnesium silicate also is stable, and garnierite and genthite form deposits where nickeliferous basic rocks are weathering. They are commonly alteration products of nickeliferous olivine. In gossans of sulphide ores nickel silicates are less common than the copper silicate, chrysocolla, which is moderately widespread in sulphide ores of copper. Garnierite has been noted as a gossan mineral of economic importance at Los

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 27, 1916.
[2] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 32, 1901.

Jarales, Malaga, Spain, where its deposits cap niccolite. Nickel sulphide is precipitated by hydrogen sulphide in neutral or alkaline but not in acid solutions. It is to be grouped with iron and zinc sulphides rather than with copper sulphides, for the latter may be precipitated either from strongly acid or strongly alkaline solutions. There is good evidence of the deposition of secondary nickel sulphides, at least in small amounts. Gersdorffite is clearly secondary in some occurrences, and, according to Kemp, secondary millerite was of economic importance in the Lancaster Gap mine, Pennsylvania. At many other places millerite occurs sparingly.

CONCENTRATION OF NICKEL SILICATES BY WEATHERING.

Before the extensive exploitation of the Sudbury deposits, in Canada (see p. 249), the ores of New Caledonia,[1] an island in the south Pacific Ocean, were the most important sources of nickel. As stated by Garland,[2] the southern half of the island of New Caledonia is composed of serpentine and schists in which serpentine predominates. The serpentine has probably been altered from a peridotite[3] relatively high in nickel. All the deposits of the nickel ore are in serpentine, but not all the serpentine contains nickel. The deposits lie high on the mountains. The serpentine is capped with red "clay" and with iron ore deposits several feet thick, consisting of nodules of hematite and oolitic gravel.[4] The iron is said to carry 4 to 8 per cent Cr_2O_3. Analyses of the red clay are stated below.

Analyses of red clay above nickel deposits in New Caledonia.

	1	2
SiO_2	18.42	12.45
Fe_2O_3	69.30	66.36
Al_2O_3	.45	.....
NiO	1.64	3.14
H_2O	9.80	12.70
MgO and MnO	.39	5.35
	100.00	100.00

It is noteworthy that so much silica and so little alumina remain in this material, whereas deposits of iron ore above serpentine in Cuba contain little silica but more alumina.

The nickel ores of New Caledonia occur, as a general rule, in irregular veins and stringers in the fissures and joints of the serpentine, ramifying in every direction and forming stockworks or net-

[1] Garnier, J., Sur la garnierite: Compt. Rend., vol. 86, p. 684, 1878.

[2] Garland, Joseph, On nickel mining in New Caledonia: Inst. Min. and Met. Trans., vol. 2, p. 121, London, 1894.

[3] Colvocoresses, G. M., Cobalt mining in New Caledonia: Eng. and Min. Jour., vol. 76, p. 816, 1903.

[4] Garland, Joseph, op. cit., p. 124.

works of small veins. The deposits are generally not more than 15 or 20 feet thick and are worked in open cuts. A few persistent veins, however, have some of the characteristics of regular lodes, extending for hundreds of feet and to moderate depths. Veins occur 2 to 3 feet thick with regular walls and dip. Locally the width of these veins increases to 4 or 5 feet.[1]

The serpentine is said to carry 0.25 to 0.75 per cent nickel. The chief mineral is garnierite, which, however, is not found as crystals. It occurs massive, botryoidal, stalactitic, and in brecciated masses. Besides garnierite there is a brown nickel-magnesium silicate or a mixture of nickel silicates and limonite. An analysis of the material by A. C. Claudet is as follows:[2]

Analysis of garnierite from New Caledonia.

Nickel oxide	12.25
Iron oxide	32.20
Magnesia	3.07
Alumina	3.62
Silica	34.80
Water at 212° F	6.43
Water above 212° F	7.07
	99.44

Specific gravity, 3.

In this analysis the nickel is only 9.64 per cent, which is less than an average of the ores. Cobalt is mined also from the serpentine. Some nickel is found with it, but, according to Garland, no cobalt with the nickel ores. Colvocoresses states that the cobalt ore, asbolane, does not occur as fissures in the serpentine but rests on it and is capped by iron oxide. It is most extensive under the broad spurs of the upland plateau. The meager descriptions available suggest a relation to an elevated and dissected peneplain.

At Nickel Mountain, near Riddle, Oreg., peridotite, consisting of olivine and enstatite, has altered to serpentine. The ores occur chiefly as flat-lying deposits on the surface of the peridotite and subordinately as veinlets in the peridotite or its decomposition product serpentine. Genthite is the only nickel mineral known to occur in these deposits.[3]

At Webster, N. C., genthite and garnierite are formed in thin, discontinuous veinlets by the decomposition of dunite, in which they occur. Specimens of dunite had the following composition.[4] Analyses 1 and 2 are by F. A. Genth; 3 is by T. M. Chatard.

[1] Garland, Joseph, op. cit., p. 125.

[2] Idem, p. 128.

[3] Kay, G. F., Nickel deposits of Nickel Mountain, Oreg.: U. S. Geol. Survey Bull. 315, p. 123, 1907.

[4] Genth, F. A., The minerals of North Carolina: U. S. Geol. Survey Bull. 74, p. 47, 1891.

Analysis of dunite from Webster, N. C.

	1	2	3
Loss by ignition	0.82	0.76	1.72
Chromite	.58	1.83	.....
SiO_2	41.89	40.74	41.58
Al_2O_3	Trace.	Trace.	.14
FeO	7.39	7.26	7.49
NiO	.35	.39	.34
MgO	49.13	49.18	49.28
CaO	.06	.02	.11
	100.22	100.18	100.66
Specific gravity	3.282	3.252	.....

At Frankenstein, in Silesia,[1] nickel ores, which are silicates, occur as nodules and veins in a red decomposition product of serpentine which caps the serpentine to moderate depths. A probable relation of the deposit to the water level is suggested by numerous cross sections given by Aschermann.

At Los Jarales, Malaga, Spain,[2] magmatic segregations of chromite, niccolite, feldspar, and augite have, by weathering, formed nickel silicate (garnierite) deposits near the surface. These consist of small irregular masses in decomposed serpentine (altered basic rock), which give way to arsenide ore at the water level.

OCCURRENCE OF NICKEL MINERALS.

Native nickel.—As would be supposed from its position in the electromotive series (p. 112), native nickel is exceedingly rare in nature. It is not unknown, however, and from its associations it is believed to have formed by magmatic segregation or by the mechanical disintegration of magmatic segregations. It is seldom pure but is generally associated with iron. Many meteoric irons contain large percentages of nickel. Pebbles in placer gravel in Josephine and Jackson counties, Oreg.,[3] contain 60 per cent of nickel. These are probably terrestrial and derived from serpentine. Small grains of similar character and probably of similar genesis are found in drift in New Zealand.[4] Several other occurrences are known. Unlike copper and silver, native nickel does not form by processes of weathering.

Morenosite, $NiSO_4.7H_2O$, is a relatively rare mineral. Being soluble it is unstable in underground waters. It is everywhere secondary and is found generally as an efflorescence. It is known near

[1] Aschermann, O. H., Beiträge zur Kenntniss des Nickelvorkommens von Frankenstein in Schlesien, 1897.

[2] Gillman, Fritz, Notes on the ore deposits of Malaga, Spain: Inst. Min. and Met. Trans., vol. 4, p. 161, London, 1896.

[3] Melville, W. H., Josephinite, a new nickel iron: U. S. Geol. Survey Bull. 113, p. 54, 1893.

[4] Skey, E., New Zealand Inst. Trans., vol. 18, p. 401, 1885.

Cape Hartegal in Galicia, Reichelsdorf in Hesse, and at a few other places. According to Coleman,[1] nickel sulphate forms on dumps of pyrrhotite-pentlandite ores at Sudbury, Ontario. These ores are subject to very rapid decay, which is attended by leaching of nickel.

Bunsenite, NiO, occurs as green octahedrons in Johanngeorgenstadt, in the Erzgebirge.

Zaratite, $NiCO_3.2Ni(OH)_2.4H_2O$, occurs as minute incrustations and is probably everywhere secondary. Nickel is precipitated by carbonate but less readily than several other common metals.[2] Zaratite is known at Texas, Lancaster County, Pa. In Cecil County, Md., a little zaratite is associated with chrome ore. Nickeliferous pyrite at Congress, Sanpoil district, Washington,[3] yields on weathering limonite and a carbonate of nickel. The oxidized ores in this deposit have a low content of nickel compared with some of the sulphide ore. Zaratite is found in the Victoria, Umtali, and Filabusi districts of Rhodesia.[4]

Garnierite, $H_2(Ni,Mg)SiO_4+aq$; *genthite*, $2NiO.2MgO.3SiO_2.6H_2O$; and other silicates are important ores of nickel, perhaps the most important after pentlandite. Nearly everywhere they are found in serpentine, associated with talc and other magnesian and nickel silicates. Their composition is indefinite, one species grading into another. At New Caledonia, a French colony of the south Pacific Ocean, garnierite forms from serpentine and the serpentine doubtless forms from the weathering of peridotite,[5] in which olivine appears to be relatively rich in nickel. An analysis of garnierite, stated by Garnier, is given below.[6]

Analysis of garnierite.

SiO_2	44.40
NiO	38.61
FeO	0.43
Al_2O_3	1.68
CaO	1.07
MnO	3.45
H_2O	10.34

Annabergite, $Ni_3As_2O_8.8H_2O$, is a fine apple-green mineral, which generally occurs as incrustations and capillary crystals and is known

[1] Coleman, A. P., The nickel industry, with special reference to the Sudbury region, Ontario, p. 20, Canada Dept. Mines, 1913.

[2] Wells, R. C., The fractional precipitation of carbonates: Washington Acad. Sci. Jour., vol. 1, p. 21, 1911.

[3] Bancroft, Howland, The ore deposits of northeastern Washington: U. S. Geol. Survey Bull. 550, p. 184, 1914.

[4] Zeally, A. E. V., Rhodesia Mus. Ninth Ann. Rept., p. 41, 1910.

[5] Colvocoresses, G. M., Cobalt mining in New Caledonia: Eng. and Min. Jour., vol. 76, p. 816, 1903.

[6] Garnier, J., Sur la garnierite: Compt. Rend., vol. 86, p. 685, 1878.

as "nickel bloom." It is found in Annaberg, Schneeberg, and other districts in the Erzgebirge. At Silver Islet, Lake Superior, and also in the Port Arthur region,[1] "nickel bloom" is associated with nickel arsenides. At Cobalt, Ontario, annabergite and its common associate erythrite, are the last minerals to form.[2] There they are obviously decomposition products of smaltite and niccolite. Where much erythrite is present, according to Miller, it masks the nickel bloom. A bright-green hydrous nickel arsenate, probably annabergite, is an important constituent of the ore of the nickel mine in Cottonwood Canyon, Humboldt County, 45 miles southeast of Lovelocks, Nev.[3] It is conspicuous in outcrops of nickel deposits in the Blackbird district,[4] Lemhi County, Idaho, where it occurs as stains and crusts. It is reported also from Silver Cliff, Colo., and Chatham, Conn.

Millerite, NiS, is usually, if not invariably, a secondary mineral. Groups of slender crystals resembling tufts of hair are common. Near St. Louis, Mo., geodes in limestone are lined with hairlike millerite. In the coal measures of South Wales millerite has been observed and ulmannite (NiSbS) is found in veins cutting limestones and other sediments in the coal measures of Durham, England.[5]

At Lancaster Gap, Pa., an amphibolite, which is probably an altered norite, carries pyrrhotite and chalcopyrite. Crusts of secondary millerite cover these minerals, according to Kemp,[6] in quantities of economic value.

Millerite is found sparingly also in the Cobalt region, where it has been observed only as hairlike crystals.[7] On the east side of Brompton Lake, Orford Township, Quebec, millerite is found with chrome garnet and calcite. It has been observed also at the Copper Cliff mine,[8] Sudbury district, Ontario, where, according to Dickson, it is secondary after pentlandite. It is known also in the nickel ores of the Erzgebirge. A little millerite is found with pyrite in the Red-

[1] Ingall, E. D., Report on mines and mining on Lake Superior: Canada Geol. Survey Ann. Rept., 1887.

[2] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, pp. 12, 19, 1913.

[3] Ransome, F. L., A reconnaissance of some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 57, 1911.

[4] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 75, 1913.

[5] Spencer, L. J., On the occurrence of alstonite and ullmanuite (a species new to Britain) in a barytes-witherite vein of the New Brancepeth colliery near Durham: Mineralog. Mag., vol. 15, p. 306, 1910.

[6] Kemp, J. F., The Lancaster Gap nickel mine: Am. Inst. Min. Eng. Trans., vol. 24, p. 620, 1894.

[7] Miller, W. G., op. cit., p. 20.

[8] Dickson, C. W., The ore deposits of Sudbury, Ontario: Am. Inst. Min. Eng. Trans., vol. 34, p. 4, 1904.

ington quicksilver mines of California,[1] and with marcasite as fine needles on the 300-foot level of the Phoenix mine, Mayacmas district, California.[2] This millerite is of uncertain origin.

Niccolite, NiAs, is a rare mineral in ore deposits of the United States. A little is found in the Gem mine, Grape Creek canyon, Colo., with bornite and rarely with native silver. It is abundant in the veins of Cobalt, Ontario,[3] where it was one of the first minerals formed and where it is one of the earliest and most characteristic minerals of the veins. Antimony may be present in place of some arsenic when it grades into breithauptite. It is present also at Silver Islet and in Port Arthur veins. A little is found with gersdorffite in the Worthington offset of Sudbury region.[4] Niccolite is found in South Lorraine district, Ontario,[5] and in the Shining Tree silver area.[6] In both these regions it is associated with native silver. At Joachimsthal, Bohemia, also niccolite is associated with native silver. At Los Jarales, Malaga, Spain, it alters to garnierite.[7]

Chloanthite, $NiAs_2$, is found in the Cobalt district, Ontario, where it is probably primary. Nodular forms were noted in La Rose mine.[8] It probably occurs in the Nickel mine[9] of Cottonwood Canyon, Humboldt County, Nev.

Gersdorffite, the nickel sulpharsenide, NiAsS, occurs in the nickel deposits of Annaberg, Schneeberg, and other districts in the Erzgebirge. A little has been noted in the Worthington offset deposit, Sudbury district, Ontario.[10] It is probably the principal unoxidized constituent of the ore of the Nickel mine, Cottonwood Canyon, Nev.[11] At some places it is without doubt a secondary sulphide. Genth describes crystals of gersdorffite from Phoenixville, Pa., incrusting secondary anglesite.[12]

At Cottonwood Canyon, near the southern boundary of Humboldt County, Nev.,[13] cobalt and nickel ores are found near a contact be-

[1] Becker, G. F., Quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, p. 286, 1888.
[2] Idem, p. 372.
[3] Miller, W. G., op. cit., p. 202.
[4] Coleman, A. P., The Sudbury nickel field: Ontario Bur. Mines Rept., vol. 14, pt. 3, p. 31, 1905. Dickson, C. W., op. cit., p. 4.
[5] Miller, W. G., op. cit., p. 140.
[6] Steinart, R. B. See Miller, W. G., op. cit., p. 190.
[7] Gillman, Fritz, Notes on the ore deposits of Malaga, Spain: Mineralog. Mag., vol. 4, p. 161, 1896.
[8] Miller, W. G., op. cit., p. 16.
[9] Ransome, F. L., Notes on some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 65, 1909.
[10] Coleman, A. P., op. cit., p. 31.
[11] Ransome, F. L., op. cit., p. 65.
[12] Genth, F. A., Contribution to mineralogy: Am. Jour. Sci., 2d ser., vol. 28, p. 248, 1859.
[13] Ransome, F. L., Notes on some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 55, 1909.

tween diorite and andesite or andesite breccia. At the Nickel mine the ore in andesitic rock occurs in narrow fissures that make various angles with the contact and are not persistent. The diorite in the footwall shows fissuring and carries stringers of quartz but no ore. The seams of nickel ore, few of them over 3 or 4 inches wide, are generally oxidized. Residual masses are partly a sulpharsenide of nickel, probably gersdorffite, and chloanthite, and other nickel minerals also are probably present, as the original ore appears to be in part a mixture of arsenides or sulpharsenides of nickel. The residual kernels of sulpharsenide are veined and coated with a bright-green hydrous nickel arsenate, probably annabergite, and this constitutes most of the ore. No quartz was noted in the veinlets. The nickel minerals are not confined to the major fissures, but, as stated by Ransome,[1] have penetrated the rock in their vicinity for several inches along joints and microscopic cracks, forming a low-grade ore. Exploration is mainly near the surface.

The Lovelock mine, about half a mile west of the Nickel mine, has shipped some high-grade nickel-cobalt ore. The country rock is altered andesite like that at the Nickel mine. The seams or veinlets of ore run in practically all directions and have no definite walls. The ore, all of which is partly or wholly oxidized, contains copper as well as nickel and cobalt. The minerals recognized are tetrahedrite, erythrite, azurite, and green crusts that may be a mixture of annabergite and brochantite.

Polydymite, Ni_4S_5, or Ni_3FeS_5, is a rare nickel sulphide reported from Grünau, Westphalia, and from Sudbury, Ontario. At the Vermilion mine, Sudbury district, it is associated with chalcopyrite and constitutes large bodies of ore.[2] On exposure it weathers with great rapidity.

Pentlandite, (Fe,Ni)S, which is probably primary in all occurrences, is the chief ore of nickel. It is found at Sudbury, Ontario, in magmatic segregations of sulphide ore,[3] in which it is intergrown with pyrrhotite.[4] The crystals being invisible to the naked eye, this material was long termed nickeliferous pyrrhotite. Pentlandite occurs with chalcopyrite at Lillehammer, Norway. Nickeliferous pyrrhotite is found at Lancaster Gap, Pa.[5]

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[1] Ransome, F. L., op. cit., pp. 57–58.

[2] Coleman, A. P., The nickel industry, with special reference to the Sudbury region, Ontario, p. 24, Canada Dept. Mines, Mines Branch, 1913.

[3] Idem, p. 29.

[4] Campbell, W., and Knight, W. E., Eng. and Min. Jour., vol. 82, p. 909, 1906.

[5] Kemp, J. F., The nickel mines at Lancaster Gap, Pa., and the pyrrhotite deposits at Anthonys Nose on the Hudson: Am. Inst. Min. Eng. Trans., vol. 24, p. 620, 1894.

COBALT.

PRINCIPAL COBALT MINERALS.

The names and chemical composition of the principal cobalt minerals are given below:

Native cobalt	Co.
Bieberite	$CoSO_4.7H_2O$.
Asbolite.[1]	
Sphærocobaltite	$CoCO_3$.
Erythrite	$Co_3As_2O_8.8H_2O$.
Linnæite.[2]	
Smaltite	$CoAs_2$.
Safflorite	$CoAs_2$.
Skutterudite	$CoAs_3$.
Cobaltite	CoAsS.

SOLUBILITIES OF SALTS OF COBALT.

The solubilities of cobalt salts are given below. The number in each square shows the number of grams of anhydrous salt held in 1,000 grams of solution as noted:

$CoSO_4$	$CoCl_2$
265.8[a]	335[b]

[a] Grams per 1,000 grams solution at 20° after Etard, Compt. Rend., vol. 113, p. 699, 1891. Landolt-Börnstein, Physikalisch-chemische Tabellen, 4th ed., Berlin, p. 465, 1912.

[b] Grams in 1,000 grams solution at 20° C. 1,000 grams water would hold 362.1 grams. Seidell, Atherton, op. cit., p. 122. Landolt and Börnstein give 333 grams at 20°.

NATURE AND OCCURRENCE OF COBALT MINERALS.

Cobalt, like nickel, is both bivalent and trivalent, but trivalent cobalt salts are readily decomposed by water, and in its natural compounds cobalt is bivalent. Cobalt sulphides are readily attacked by ferric sulphate solutions.[3] The sulphate and chloride are highly soluble. The sulphate, being soluble, is unstable in ore deposits, but the oxide, in absence of strong solvents, will endure. Asbolite, composed of cobalt and manganese oxides, is an important source of cobalt and forms the chief ore of cobalt in cobalt deposits of New Caledonia. I know of no silicate corresponding to garnierite of the nickel series. The carbonate, which is not a common mineral, is probably secondary. In the presence of arsenic cobalt ores on oxidation yield erythrite, or cobalt bloom. Linnæite is a valuable con-

[1] Earthy hydrated oxides of Co and MnO_2.

[2] A combination of cobalt and sulphur with iron, nickel, and copper; composition uncertain.

[3] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 82, 1901.

stituent of the lead-nickel-cobalt ores of the Mine Lamotte area, Missouri, which replace limestone.[1]

As cobalt sulphide is formed by hydrogen sulphide in alkaline solutions or with alkaline sulphide reacting with cobalt sulphate, the sulphide enrichment of cobalt ores appears to be probable, but it has been the subject of but little experimental study, and few paragenetic data are available.

Native cobalt.—Pure native cobalt is unknown. Perhaps it exists in some meteoric nickel irons. About 1 per cent of cobalt is present in some natural nickel irons of Del Norte County, Cal., and Josephine County, Oreg.[2] These are probably magmatic segregations.

Bieberite, $CoSO_4.7H_2O$, is an alteration product of cobalt sulphides, so called from Bieber in Hesse. It generally occurs as stalactites and crusts. The walls and fractures in some Cripple Creek mines are coated with hairlike crystals and crusts of a pink substance containing cobalt sulphate.[3]

Pink efflorescent salts lining a prospect tunnel entering sandstones impregnated with copper sulphides in White Canyon, 15 miles east of Hite, Utah, carry cobalt, possibly in the form of bieberite.[4]

Asbolite is a hydrated oxide of uncertain composition, in which are oxides of manganese and cobalt, the latter in some specimens as high as 32 per cent. It is associated with the nickel-bearing rocks of New Caledonia, where it is a decomposition product of serpentinized peridotite.[5] It was common in the deposits of the Mine Lamotte area, Missouri.[6] Asbolite is found in stemlike forms, spots, and beds in Tertiary sands at Wolwuwe-Saint-Lambert, near Brussels.[7] It occurs in considerable quantity in the outcrop of some of the Cobalt, Ontario, veins[8] and was found also in Cornwall and at Cheshire, Scotland,[9] and it is known in numerous ore deposits in New South Wales[10] and elsewhere.

Sphærocobaltite, $CoCO_3$, occurs as small spheroid masses in Schneeberg, Saxony. Its genesis is uncertain. The trigonal mineral "kobaltspat" from this locality carries ferric iron and some lime.[11]

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[1] Keyes, C. R., A report on Mine Lamotte sheet: Missouri Geol. Survey, vol. 9, pt. 4, p. 82, 1896.

[2] Melville, W. H., Josephinite, a new nickel iron: U. S. Geol. Survey Bull. 113, p. 54, 1893.

[3] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 126, 1906.

[4] Hess, F. L., written communication.

[5] Glasser, E., Rapport sur les richesses minérales de la Nouvelle Calédonie: Annales des mines, vol. 5, pp. 503–701, 1904.

[6] Keyes, C. R., A report on Mine Lamotte sheet: Missouri Geol. Survey Rept. No. 4, vol. 9, p. 82, 1895.

[7] Crocq, J., Cobalt in the sands of Wolwuwe-Saint-Lambert: Chem. Soc. Jour., vol. 70, pt. 2, p. 434, London, 1896; digest translation from Acad. roy. sci., lettres et beaux-arts Belgique Bull., vol. 3, pp. 485–498, 1894.

[8] Hewett, D. F., oral communication.

[9] Collins, J. H., A handbook to the mineralogy of Cornwall and Devon, p. 11, 1871.

[10] Pittman, E. F., The mineral resources of New South Wales: New South Wales Geol. Survey, p. 223, Sydney, 1901.

[11] Leitmeier, H., in Doelter, C., Handbuch der Mineralchemie, Band 1, p. 442, 1912.

Remingtonite, a cobalt carbonate,[1] is found in a copper mine near Finksburg, Carroll County, Md. It coats thin veins of serpentine in hornblende-epidote rock.

Erythrite, $Co_3As_2O_8.8H_2O$, the reddish or flesh-colored cobalt arsenate, is a common surface decomposition product of arsenical cobalt ores and is known as cobalt bloom. It is probably confined to alteration zones. In the region of Cobalt, Ontario, it is regarded as a surface indication of cobalt and silver ores of that area. In the Blackbird district,[2] Lemhi County, Idaho, crusts of erythrite on outcrops are so conspicuous as to be seen at a distance of half a mile. It occurs in nickel and cobalt ores in Cottonwood Canyon and Humboldt County, Nev.,[3] and in a vein carrying a number of rare metals near Placerville, Colo.[4]

Erythrite is found also at Schneeberg, Saxony, and elsewhere in the Erzgebirge. At Cobalt, Ontario, it occurs in cracks and druses, and with annabergite it is the latest mineral formed, later even than native silver.[5] It is searched for diligently as an indication of silver ores in the eastern Ontario district. Cobalt bloom with sulphide minerals is found in Casey Township[6] and in the area west of Bay Lake[7] on Montreal River; at Florence Lake;[8] in the Shining Tree area;[9] in the region of Port Arthur and at Silver Islet. It is found in oxidized parts of nearly all cobalt-bearing veins.

Smaltite, $CoAs_2$, corresponds to the nickel diarsenide chloanthite. It is probably always primary. It is found at Joachimsthal, Bohemia; in many veins of Cornwall; at Junaberg, Sweden; Cobalt, Ontario; and elsewhere. Near Gothic, Gunnison County, Colo., it is associated with erythrite and native silver in calcite gangue.[10]

Near Comer, Oreg., it is found in a gold and silver bearing vein with chalcopyrite and pyrite. Near the junction of the Kruis and Selons rivers, Transvaal, are smaltite veins, one of which carries 1.4 to 4 ounces of gold per ton. Smaltite generally contains a little sulphur and grades into cobaltite.

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[1] Boothe, J. C., On remingtonite, a new cobalt mineral: Am. Jour. Sci., 2d ser., vol. 14, p. 48, 1852.

[2] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 77, 1913.

[3] Ransome, F. L., Notes on some mining districts in Humboldt County, Nev.: U. S. Geol. Survey Bull. 414, p. 55, 1909.

[4] Hess, F. L., Notes on vanadium deposits near Placerville, Colo.: U. S. Geol. Survey Bull. 530, p. 151, 1913.

[5] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, pp. 12, 17, 1913.

[6] Hore, R. F. See Miller, W. G., op. cit., p. 145.

[7] De Lum, J. S. See Miller, W. G., op. cit., p. 154.

[8] Collins, W. H. See Miller, W. G., op. cit., p. 194.

[9] Stewart, R. B. See Miller, W. G., op. cit., p. 187.

[10] Sanford, Samuel, and Stone, R. W., Useful minerals of the United States: U. S. Geol. Survey Bull. 585, p. 49, 1914.

Cobaltite, CoAsS, is probably primary. It occurs at Junaberg, Sweden; in Westphalia; Cornwall, etc. At Cobalt it is associated with smaltite.[1]

TITANIUM.

The principal titanium minerals are listed below:

Brookite	TiO_2.
Octahedrite	TiO_2.
Rutile	TiO_2.
Titanite (sphene)	$CaTiSiO_5$ ($CaO.TiO_2.SiO_2$).
Ilmenite	$FeTiO_3$.
Picrotitanite	$(Fe,Mg)TiO_3$.
Perofskite	$CaTiO_3$.

Titanium is grouped in the periodic system with zirconium, cerium, and thorium, all of which are quadrivalent. Titanium is very feebly acid forming and feebly base forming. Titanium is common in the economy of nature; of 800 rocks analyzed in the laboratory of the United States Geological Survey, 784, according to Clarke,[2] contained titanium. Clarke estimates that known terrestrial matter contains 0.46 per cent titanium. The principal titanium minerals are titanite, ilmenite, rutile, and perofskite, all of which are found in igneous rocks. None of these are known certainly to be products of surface alteration except possibly titanite. The alteration products, titanomorphite or leucoxene, are said to have the composition of titanite ($CaTiSiO_5$).

Doelter[3] states that rutile is fairly soluble in water, but this statement may well be questioned. (See p. 399.) All of the titanium minerals are probably insoluble in water and in weak acid solutions. Ilmenite and titanite are slowly dissolved, however, in fairly concentrated hydrochloric acid; and perofskite is decomposed by boiling sulphuric acid. Without doubt titanium is dissolved by some natural solvents, since Wait[4] reports it in the ash of many plants. An ash of oak is reported to have carried 0.31 per cent and the ashes of many coals carry nearly 1 per cent. All the titanium minerals, however, are so nearly insoluble that appreciable concentrations in the secondary zones by solution and reprecipitation are rare.

Brookite, TiO_2 (orthorhombic), appears to be nearly if not altogether an alteration product. It occurs in igneous rocks, in gneiss, and in crystalline limestone. At Magnet Cove, Ark., brookite has altered to rutile. Pseudomorphs of brookite after titanite are found at St. Philippe in the Vosges.

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[1] Miller, W. G., op. cit., p. 20.

[2] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 21, 1916.

[3] Doelter, C., Min. pet. Mott., vol. 11, p. 325, 1890.

[4] Wait, C. E., Am. Chem. Soc. Jour., vol. 18, p. 403, 1896.

Octahedrite, TiO_2 (tetragonal), according to F. W. Clarke,[1] is always formed by the alteration of other titanium minerals. It forms readily in processes of hydrothermal alteration and possibly is a product of weathering. Octahedrite is found in igneous, sedimentary, and metamorphic rocks. It was recently described by Knopf in gold-platinum ore from the Boss mine, Yellow Pine district, Nevada, where it is associated with quartz, precious metals, and rutile.[2] Octahedrite occurs also in tin mines of Saxony and with brookite at many places in the Alps.[3] It is a product of the alteration of ilmenite or titanite in wall rocks of veins formed at moderate depths, for example, at Freiberg, Nagyag,[3] and at Silver Cliff, Colo.

Rutile, TiO_2 (tetragonal), is a common constituent of igneous rocks and of gneisses, mica schists, and other metamorphic rocks. It is found also in pegmatites, contact-metamorphic deposits, and in veins of the deep zone. An unusual dike in Nelson County, Va.,[4] is composed of rutile and apatite. At Ducktown, Tenn., rutile crystals, somewhat rounded, are weathered out of graywacke and may be picked up on the surface. It occurs at the surface also at Magnet Cove, Ark. It is found also near St. Peter's Dome, Pikes Peak district, Colorado. Rutile is common in certain of the auriferous deposits of the Juneau gold belt,[5] Alaska, in veins that contain albite, quartz, and calcite. Some of it occurs in drusy cavities. Rutile is found associated with quartz, octahedrite, gold, and platinum in the Boss mine, Yellow Pine district, Nevada.[6]

Although rutile as a vein filling appears to be characteristic of deposits formed at high temperatures, it is nevertheless a common alteration product of ilmenite and titanite in wall rocks of veins formed at moderate depths. Lindgren[7] states that it occurs in nearly all hydrothermally metamorphosed rocks.

Titanite, $CaTiSiO_5$, sphene, is a common rock-making mineral in igneous rocks, both acidic and basic. It is found also in pegmatites and in contact-metamorphic deposits; and, according to Stelzner, is intergrown with tourmaline and quartz in copper veins of Las Condes, Chile.[8] On alteration it loses color and passes into an earthy

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 352, 1916.

[2] Knopf, Adolph, A gold-platinum-palladium lode in southern Nevada: U. S. Geol. Survey Bull. 620, p. 7, 1915.

[3] Koenigsberger, J., Transformations and chemical reactions in their application to temperature measurements of geological occurrences (translated by J. A. Ambler): Econ. Geology, vol. 7, p. 697, 1912.

[4] Watson, T. L., and Taber, Stephen, The Virginia rutile deposits: U. S. Geol. Survey Bull. 430, p. 200, 1910.

[5] Spencer, A. C., The Juneau gold belt, Alaska: U. S. Geol. Survey Bull. 287, p. 33, 1906.

[6] Knopf, Adolph, A gold-platinum-palladium lode in southern Nevada: U. S. Geol. Survey Bull. 620, p. 7, 1905.

[7] Lindgren, Waldemar, Metasomatic processes in fissure veins: Am. Inst. Min. Eng. Trans., vol. 30, p. 603, 1900.

[8] Stelzner, A. W., Ueber die Turmalinführung der Kupfererzgänge von Chile: Zeitschr. prakt. Geologie, vol. 5, p. 44, 1897.

mass with calcite. It alters also to rutile and octahedrite.[1] At Green River, N. C., crystals of titanite are altered pseudomorphously to xanthitane, possibly a hydrous aluminum titanite.[2]

Titanomorphite is a mossy granular alteration product of rutile and ilmenite. According to Catherein,[3] it is essentially titanite with some rutile. Leucoxene, a white, flocculent alteration product of titanium minerals, was formerly supposed to have the composition of titanite, but this is uncertain. It is now believed to have a variable composition.

Ilmenite, $FeTiO_2$, is a common constituent of igneous rocks, both acidic and basic, and is in many places associated with magnetite. It is found also in pegmatites, in contact-metamorphic rocks, in deposits of the deep-vein zones, and in dynamically metamorphosed rocks. It is a large constituent of the titaniferous iron ores[4] that are widely distributed in the United States, in which it is intergrown microscopically with magnetite.

Ilmenite has been formed synthetically[5] with magnetite by heating iron dust, ferric oxide, and amorphous titanic oxide with hydrofluoric acid in a platinum tube at 270° to 300° C. This experiment with a reducing agent, iron, is noteworthy because ilmenite appears to be unstable in wall rocks along veins formed at moderate depths by hot solutions. Near such veins it is commonly altered to rutile.[6] Ilmenite alters also to leucoxene or titanite.

Perofskite, $CaTiO_3$ occurs in both igneous and metamorphic rocks, particularly in basic and alkaline igneous rocks. It is found also in pyroxene gneiss and in chloritic and talcose metamorphic rocks. It has been noted as an alteration product of titanite in phonolite at Klein Priesen, Bohemia.[7]

ALUMINUM.

ALUMINUM MINERALS.

Aluminum is abundant in the crust of the earth and is a constituent of many rock-making minerals. According to F. W. Clarke,[8] it forms 7.96 per cent of the average of analyzed igneous rocks and it is present in considerable abundance in many sedimentary rocks,

[1] Iddings, J. P., Rock minerals, p. 491, 1911.

[2] Eakins, L. G., Mineralogical notes: U. S. Geol. Survey Bull. 60, p. 135, 1890.

[3] Catherein, A., Ueber Titaneisen, Leukoxen, und Titanomorpheit: Zeitschr. Kryst. Min., vol. 6, p. 244, 1882.

[4] Singewald, J. T., jr., The titaniferous iron ores in the United States: U. S. Bur. Mines Bull. 64, 1913. Kemp, J. F., The titaniferous iron ores of the Adirondacks: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 377, 1899. Newland, D. H., Geology of the Adirondack magnetic iron ores: New York State Mus. Bull. 119, p. 146, 1908.

[5] Bruhns, W., Beiträge für Mineralsynthese: Neues Jahrb., 1889, Band 2, p. 65.

[6] Lindgren, Waldemar, Metasomatic processes in fissure veins: Am. Inst. Min. Eng. Trans., vol. 30, p. 603, 1900.

[7] Iddings, J. P., Rock minerals, p. 495, New York, 1911.

[8] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 27, 1916.

particularly in shales and limestones. A list of all the minerals that contain aluminum is too long to be given here. Some that are important in protore or as ores of aluminum or as gangue minerals in deposits of other metals are listed below.

Diaspore	$Al_2O_3.H_2O$.
Gibbsite	$Al_2O_3.3H_2O$.
Bauxite	$Al_2O_3.2H_2O$.
Alunite	$K_2O.3Al_2O_3.4SO_3.6H_2O$.
Kaolin	$Al_2O_3.2SiO_2.2H_2O$.
Sericite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$.
Feldspars	Variable.
Nepheline	$NaAlSiO_4$.

Aluminum, which is always trivalent, behaves in weathering like the trivalent metals, iron and chromium. The oxides of all three of these metals are comparatively stable in earth waters, particularly in alkaline waters. Thus the oxides corundum, magnetite, hematite, and chromite are commonly segregated near the surface and their deposits are enriched by removal of material that is more soluble. But each of these metals is dissolved somewhat more readily in acid waters. Aluminum sulphate is highly soluble in slightly acid solutions, and aluminum, like iron, is commonly present in sulphuric acid mine waters, but is not reported in alkaline waters. There is no native metal ore or carbonate of aluminum. Aluminum acts as an acid-forming element (as in $Al_2(SO_4)_3$), and also as a base-forming element (as in Na_3AlO_3). Although both of these salts are hydrolyzed in water, the latter is much more readily hydrolyzed. Thus when alkaline solutions leach aluminous material compounds not containing aluminum may be removed, while aluminum remains as kaolin or hydrous oxide. An extreme case is where nepheline syenites or other alkali-rich aluminous rocks are altered to form a mantle rock of bauxite. The alkaline carbonates and probably other alkalies have removed silica and alkaline earths, greatly enriching the mantle in aluminum, thus:

$$2NaAlSiO_4+2H_2CO_3+3H_2O= Al_2O_3.2H_2O+H_2Na_2(CO_3)_2+2H_2SiO_3.$$

Where sulphuric acid reacts on aluminous rocks or minerals the aluminum may be concentrated somewhat as kaolin by the removal of substances leached out more readily than aluminum. The concentration, however, generally does not yield a deposit so rich in aluminum as the bauxite mantle mentioned above. On the other hand, aluminum in sulphide ores is itself removed by sulphuric acid along with iron, zinc, copper, alkaline earths, and alkalies, but it is more stable than any of these except iron, and in strong acid kaolin is more stable than oxides of iron. Where deposits of iron sulphides are disseminated in igneous rocks, such as diorite or monzonite, such

rocks on weathering may yield a mantle of kaolin only slightly stained with iron. By long-continued action, however, even kaolin will break down, forming a siliceous capping at the surface and extending down a few inches below. This relation is conspicuously shown at Cananea, Mexico.

For preparing commercial aluminum sulphate kaolin is treated with strong sulphuric acid:

$$H_2Al_2(SiO_4)_2.H_2O+3H_2SO_4=Al_2(SO_4)_3+2H_2SiO_3+3H_2O.$$

The sulphate is removed by filtration from the silicic acid residual. Although heat and strong acid are employed in the commercial application of the reaction, it probably takes place slowly at some places in warm, arid climates in forming the mantle of igneous rocks carrying disseminated sulphide ores. The importance of these relations would justify close study of the problem in the field and laboratory, for the siliceous capping may be regarded as a kind of outcrop or surface indication of a deposit containing a sulphide.

In the equation stated above, where the kaolin is leached by sulphuric acid, aluminum is leached out and silica remains behind. But in the reaction where nepheline is attacked by carbonic acid a strong alkali is released and in this solution silica would be removed. It is noteworthy that these types of alteration do not go on, at least not nearly to completion, except at very shallow depths. At greater depths kaolin is formed by acid and possibly by some alkaline solutions reacting on feldspars, mica, and other aluminum minerals.

In deposits of sulphide ore the aluminum minerals are chiefly of interest as gangue minerals. They do not supply much ore for the extraction of the metal, although some lodes have supplied china clays, and the cryolite deposits of Greenland, which are clearly primary, contain small amounts of metallic sulphides. Bauxite, the chief ore of aluminum, is formed by surface decay of aluminous rocks.

CONCENTRATION OF ALUMINUM BY WEATHERING.

The superficial concentration of bauxite is closely analogous to that of iron oxide, and in some deposits both are found together. Both oxides also are commonly pisolitic in secondary deposits. As iron is concentrated from dunite, peridotite, or greenalite and siderític rocks, so bauxite is concentrated from nepheline syenite, clayey limestone, and other rocks rich in aluminum, and particularly from those that supply abundant alkalies to aid solutions removing silica.

In Saline County, Ark.,[1] intrusive masses of nepheline syenite are covered by Tertiary gravels. Bauxite deposits with an average

[1] Hayes, C. W., The bauxite deposits of Arkansas: U. S. Geol. Survey Twenty-first Ann. Rept., pt. 3, p. 446, 1901. Mead, W. J., Occurrence and origin of the bauxite deposits of Arkansas: Econ. Geology, vol. 10, p. 28, 1915.

thickness of 11½ feet rest on the nepheline syenite. The lower parts of the bauxite deposits show alumina skeletons, pseudomorphic after the nepheline and feldspar of the syenite. The upper parts of the deposits are generally pisolitic. The cappings of the syenite bodies, as shown by Meade, have obviously been altered by superficial processes. Alkalies, silica, and other elements have been removed, and the remaining alumina has thereby become concentrated. In the upper 2 feet at the surface silica is concentrated.

In the southern Appalachians, in a narrow belt[1] about 60 miles long, extending southwestward from Adairsville, Ga., through Rome, Ga., and Rock River, Ala., bauxite deposits are found here and there in a residual mantle 100 feet or more thick, which rests on sedimentary rocks, mainly on Knox dolomite. Thrust faults are numerous; no igneous rocks are present. It is not certain that the alumina has concentrated by simple processes of weathering from materials in the dolomite or in a sandy shale that was deposited above the dolomite. Below the dolomite is a heavy bed of aluminous (Conasauga) shale, and Hayes suggests that waters ascending along faults have dissolved alumina from the shales and precipitated it near the surface. The origin of these deposits and their connection with faulting are, however, still in doubt. Near Keenesburg, Carter County, Tenn., bauxite is found as a large, irregular, deep pocket in residual material resulting from decomposition of Knox dolomite.[2] Other deposits in Tennessee are probably residual also and appear to be generically similar to those in the Alabama and Georgia belt.

In Georgia, about 30 miles east of Macon, bauxite is mined[3] near the contact between the Tuscaloosa (Lower Cretaceous) and Claiborne (Tertiary) formations, which are made up chiefly of flat-lying unconsolidated clays and sands. The bauxite deposits rest directly on the Cretaceous clays or are nodules disseminated through them. Some beds are 10 feet thick.

Kaolinite is the commonest product of weathering of aluminum minerals, such as feldspars and mica. Nearly all igneous rocks contain aluminum minerals, and kaolinite is almost invariably formed as a result of their weathering. Limestones likewise generally contain aluminum as kaolinite, and by weathering form residual clays. Shales are clays that have been consolidated by pressure. On weathering they break down and again form clays. If a surface has long

[1] Hayes, C. W., The geological relations of the southern Appalachian bauxite deposits: Am. Inst. Min. Eng. Trans., vol. 24, p. 243, 1894; also Hayes, C. W., Geology of the bauxite region of Georgia and Alabama: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 3, p. 547, 1895.

[2] Phalen, W. C., Bauxite and aluminum: U. S. Geol. Survey Mineral Resources, 1912, pt. 1, p. 951, 1913.

[3] Veatch, Otto, Second report on the clay deposits of Georgia: Georgia Geol. Survey Bull. 18, p. 430, 1909.

been exposed to weathering with little erosion, as in a country that is approaching base-level soluble substances are almost completely leached out and the residual clay remains. Ordinarily the parent rock may be found a few feet, or rarely more than 50 or 100 feet, below the surface. Such clayey substance or mantle rock commonly constitutes the soils of old unglaciated surfaces. Even the sandstones and quartzites contain some clay, and their residual soils may be more aluminous than the parent sandy rocks.

Although new mineral combinations result from hydrothermal processes attending the deposition of lode ores, there is little evidence that much aluminum is carried into the veins by ascending hot solutions, for aluminum compounds are rare in veins contained in non-aluminous rocks. Cold sulphuric acid solutions dissolve aluminum from its compounds fairly readily, as is indicated above. There is but little evidence, however, that aluminum compounds are extensively precipitated in open spaces from cold acid waters. Some alunitic veinlets are secondary and some kaolin is deposited in fractures by descending solutions, but in most deposits the larger proportion of the secondary aluminous gangue appears to be a residual product of altered feldspar, sericite, and other minerals. Without much doubt aluminum, like iron, is carried out of sulphide ore bodies in great quantities, for the slimes precipitated from mine waters commonly contain large proportions of hydrous aluminum compounds.

OCCURRENCE OF ALUMINUM MINERALS.

Gibbsite, bauxite, and diaspore.—Gibbsite, $Al_2O_3.3H_2O$, bauxite, $Al_2O_3.2H_2O$, and diaspore, $Al_2O_3.H_2O$, are hydrated aluminum oxides corresponding to the hydrous iron oxide series. By extreme weathering, especially in moist, hot climates, these minerals are formed from aluminum silicates.[1] They have been reported from comparatively few ore veins, and those in which they have been identified are almost without exception of late Tertiary age. It is believed that they have been formed in some deposits very near the surface by reactions upon aluminum silicates.[2] In the altered rhyolite of the Rosita Hills, Colo.,[3] diaspore is associated with alunite, quartz, and kaolin, and in altered latite near Silverton, Colo.,[4] with alunite

[1] Worth, H. and F. J., Geol. Mag., 1903, p. 154. Worth, H., Mineralog. Mag., vol. 13, p. 172, 1902.

[2] Hayes, C. W., Geology of the bauxite region of Georgia and Alabama: U. S. Geol. Survey Sixteenth Ann. Rept., pt 3, p. 547, 1895; The geological relations of the southern Appalachian bauxite deposits: Am. Inst. Min. Eng. Trans., vol. 24, p. 243, 1894.

[3] Cross, Whitman, Geology of Silver Cliff and the Rosita Hills, Colo.: U. S. Geol. Survey Seventeenth Ann. Rept., pt. 2, pp. 316–317, 1896.

[4] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: U. S. Geol. Survey Bull. 182, pp. 121–124, 1901.

and kaolin. Microscopic crystals of diaspore have been identified at several places in the alunitic-kaolinic veins of Goldfield, Nev.[1]

Alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$, is a white or faintly pink mineral which in some of its occurrences closely resembles kaolin and sericite. It is formed from either hot or cold solutions. It is not known to have formed under high temperature and great pressure. The alunitic deposits of Goldfield, Rabbit Hole, and Alunite, Nev., and of the Rosita Hills and Rico, Colo., have been formed presumably by hot ascending waters mixed with oxygenated surface waters. The alunitic veinlets at Cripple Creek, Colo.,[2] and at Clifton-Morenci, Ariz.,[3] and the "Chinese talc" of Leadville, Colo., have probably been deposited by descending cold sulphate waters. Alunite is commonly associated with kaolin, and the ranges of the two minerals are probably closely similar. Alunite is much less soluble than some other sulphates of aluminum and is therefore relatively stable in oxygenated solutions. The occurrence and genesis of alunite have recently been discussed by Butler and Gale.[4]

Kaolin, $Al_2O_3.2SiO_2.2H_2O$, is a common product of rock alteration at and near the surface.[5] It forms where aluminum silicates are leached by ground water that contains either carbonate or sulphuric acid. It is generally abundant in the oxidized zone and is commonly present in the zone of enrichment in sulphide ore deposits. As a primary vein constituent it is exceedingly rare. At Goldfield, Nev., according to Ransome,[6] it was probably deposited simultaneously with alunite and gold by ascending thermal waters, partly oxidized to sulphate. In several other districts, as at the Rosita Hills, Colo., and Rabbit Hole, Nev., it is associated with alunite and commonly with diaspore or other hydrous aluminum oxides. According to Gregory,[7] the deposits of kaolin or china clay of Cornwall and Devon extend to the bottom of some deep mines and probably to greater depths. These he regards as having been formed by solutions containing boric and fluoric acids. Hickling,[8] however, regards the

[1] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 125, 1909.

[2] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 125, 1906.

[3] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 119, 1905.

[4] Butler, B. S., and Gale, H. S., Alunite, a newly discovered deposit near Marysvale, Utah: U. S. Geol. Survey Bull. 511, 1912.

[5] Lindgren, Waldemar, The relation of ore deposition to physical conditions: Econ. Geology, vol. 2, p. 120, 1907. Ransome, F. L., Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 212, 1910; discussion by S. F. Emmons, idem, p. 477.

[6] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 192, 1909.

[7] Gregory, J. W., Criteria of downward sulphide enrichment (discussion): Econ. Geology, vol. 5, p. 680, 1910.

[8] Hickling, George, China clay; its nature and origin: Inst. Min. Eng. Trans. (England) vol. 36, p. 24, 1909.

kaolin of Cornwall as entirely secondary. Stremme states[1] that kaolin deposits are formed mainly by action of organic agencies, principally by "moorwasser," although he admits other methods of the formation of kaolin. Rösler[2] considers pneumatolytic agencies to be the effective ones.

It has been shown that precipitation of copper sulphide may liberate sulphuric acid, which is available for kaolinization of sericite or feldspar or other aluminum minerals, and consequently kaolin is commonly an associate of secondary chalcocite and covellite in aluminous rocks. At Butte, Mont., according to S. F. Emmons,[3] kaolin associated with secondary copper sulphides was found 1,100 feet deep in the East Gray Rock mine, and Kirk[4] also has reported it at great depths. It is abundantly developed in the oxidized ores at Bisbee, Ariz.,[5] and probably also with chalcocite ores. It is not uncommon as a secondary product at Morenci, Ariz.,[6] where, according to Lindgren, it is not formed during the sericitization of the porphyry which accompanied the formation of the pyritic veins, but it accompanies in small amounts the chalcocite in the veins in porphyry and the copper carbonates in decomposed deposits in limestone. It occurs as veinlets in the quartz of several mines and as large masses in the Longfellow mine, where it is adjoined by limonite. Pure white kaolin commonly occurs also with azurite. According to Lindgren,[7] its formation in limestone may be explained by the action of aluminum sulphate on free silica in the presence of cupric sulphate:

$$Al_2(SO_4)_3+3CuSO_4+3CaCO_3+2SiO_2+6H_2O= 3CuO.2CO_2.H_2O+H_4Al_2Si_2O_9+3CaSO_4+3H_2SO_4+CO_2.$$

At Georgetown, Colo., according to Spurr, Garrey, and Ball, kaolin is crystallized in vugs. Weed also notes crystals lining vugs in Butte veins.

Kaolinic ores are commonly rich in gold and silver. A noteworthy example is seen at the Montgomery Shoshone mine of the Bullfrog district, Nevada, where the richer ores were found in altered claylike rhyolite. At many places rich kaolinic secondary ores of

[1] Stremme, H., Über Kaolinbildung: Zeitschr. prakt. Geologie, vol. 16, pp. 122, 443, 1908.

[2] Rösler, H., Beiträge zur Kenntniss einiger Kaolinlagerstätten: Neues Jahrb., Beilage Band 15, p. 231, 1902; Über Kaolinbildung: Zeitschr. prakt. Geologie, vol. 16, p. 251, 1908.

[3] Emmons, S. F., The secondary enrichment of ore deposits, in Pošepný, Franz, The genesis of ore deposits, p. 443, 1902.

[4] Kirk, C. T., Conditions of mineralization in the copper veins at Butte, Mont.: Econ. Geology, vol. 7, p. 35, 1912.

[5] Ransome, F. L., The geology and ore deposits of Bisbee, Ariz.: U. S. Geol. Survey Prof. Paper 21, pp. 32, 147, 1904.

[6] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 111, 1905.

[7] Idem, p. 193.

silver are extensively developed—for example, in the Broken Hill lode, Australia,[1] and in the Mount Morgan vein, Queensland.

Sericite.—Of the vein minerals that carry aluminum, sericite is perhaps the most common. It is formed in the main as a pseudomorphous replacement of feldspar or other aluminous silicates. In some replacement veins it is very abundant and was probably formed by ascending thermal waters, although there is much evidence that it forms also by processes of hydrometamorphism[2] that are independent of processes of ore deposition. Hickling[3] states that sericite is an intermediate product of the kaolinization of potash feldspar exposed to atmospheric weathering. Paige[4] mentions an occurrence near Tyrone, N. Mex., where veinlets containing sericite cut turquoise, which he regards as a product of weathering. There is little evidence, however, that sericite forms extensively under the conditions that prevail where secondary sulphides are deposited.

Feldspars.—Of the feldspars, albite and adularia are primary gangue minerals of ore veins. Albite is generally formed at considerable depth; adularia nearer the surface. Neither feldspar is known to form in cold solutions by processes of secondary alteration, although adularia, according to Lindgren,[5] may be deposited at or near the surface, where the temperature could not have been much above 100° C.

GANGUE MINERALS.

NATURE AND GENESIS.

Among the minerals found in metalliferous sulphide ores are many that are formed by processes of surface alteration only. These include a large number of the native metals, carbonates, silicates, oxides, and some other compounds. Among the sulphides not one is known to be formed exclusively by secondary processes, although several are secondary in nearly all their known deposits. On the other hand, the primary ores include several sulphides that are practically unknown as secondary minerals. A list of such sulphides should include arsenopyrite, bismuthinite, molybdenite, pyrrhotite, and probably others.

The data concerning the genesis of many minerals are inconclusive, and to determine the origin of an ore one must generally rely on paragenesis and mineral association rather than on the occurrence

[1] Clark, Donald, Australian mining and metallurgy, p. 347, 1904.

[2] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 125, 1905.

[3] Hickling, George, China clay; its nature and origin: Inst. Min. Eng. Trans. (England), vol. 36, pp. 10, 24, 1909.

[4] Paige, Sidney, The origin of turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 7, p. 382, 1912.

[5] Lindgren, Waldemar, Metasomatic processes in fissure veins, in Pošepný, Franz, The genesis of ore deposits, p. 532, 1902.

of isolated species. So far as they may serve as an indication of the genesis of the ore, the gangue minerals are perhaps as important as the sulphides.

It is difficult to draw sharp distinctions between gangue and ore minerals, and neither of these terms is uniformly used with the same meaning. The gangue minerals are commonly distinguished as the earthy or nonmetallic minerals associated with the metalliferous minerals in the ore. As commonly used the term gangue does not include all minerals without metallic luster, nor does it exclude all minerals that contain metals. The iron-bearing silicates are almost universally regarded as gangue minerals in deposits of metals other than iron.

In the table below the minerals listed are primary. Probably none of these are formed by processes of superficial alteration and enrichment. Most of them are nonmetallic or gangue minerals.

Some minerals which are not formed by processes attending superficial enrichment of ores.

Acmite.	Diopside.	Rhodonite?
Actinolite.	Emery.	Rutile.
Adularia.	Garnet.	Scapolite.
Albite.	Graphite.	Sillimanite.
Allanite.	Hornblende.	Spinel.
Amphiboles.	Humites.	Tourmaline.
Anhydrite.	Ilmenite.	Tremolite.
Augite.	Ilvaite.	Vesuvianite.
Biotite.	Lepidolite.	Wollastonite.
Chromite.	Microcline.	Zircon.
Corundum.	Orthoclase.	Zoisite.
Cryolite.	Pyroxenes.	

A number of gangue minerals are formed by processes of weathering and hydrometamorphism. Many of them are alteration products or replacements of older gangue minerals, but some are reprecipitated in open fissures. The term hydrometamorphism is used to define those changes which take place through the agency of surface waters at depths somewhat below the oxidizing zones—possibly at horizons where the waters have become neutral or alkaline. Several silicates are developed by such processes, among them chlorite, epidote, muscovite, quartz, serpentine, and talc. Of these minerals all except talc are formed also under some conditions by ascending thermal waters.

SILICA.

It is assumed that ascending hot waters are alkaline solutions. If they were acid at their sources they would tend to become alkaline by reactions with wall rocks composed largely of alkaline

silicates. Although the alkalies are generally regarded as its natural solvents, silica is dissolved also by acid waters. The amount, though small, is appreciable even in solutions that give strongly acid reactions, and all but three of the samples of water whose analyses are given on pages 87 to 89 carried silica. The silica in dilute acid waters is generally assumed to be mainly or altogether in the colloidal state. It would be supposed that the quantity of silica in solution would increase with that of the carbon dioxide, but a survey of the analyses does not show this, nor is the increase in the quantity of alkalies with increase of silica very pronounced. The water that is richest in silica is a strongly acid water of the Comstock lode. (See p. 88.)

The secondary metal-bearing silicates, chrysocolla, calamine, and many others, have already been discussed. Some of these are formed probably in the presence of acid solutions, and to judge from their mineral associations the various forms of hydrated silica, such as chalcedony and chert, may be formed under similar conditions.

In some ore bodies clear crystalline quartz appears to have been deposited by cold descending waters. Some of the disseminated ores of southeastern Missouri carry 5 per cent quartz, and an appreciable amount of silica is present in the sulphate-carbonate waters of the mines of that region. The mine waters[1] carry considerable quantities of alkalies and alkali earths and give an alkaline reaction. Certain quartzose ore deposits have been regarded as the results of enrichment or concentration by downward-moving waters, and clear crystalline quartz is found in geodes remote from igneous intrusives and forms the interstitial filling of sandstones that have been converted into quartzites.

In the zinc deposits of southwestern Wisconsin, which were formed presumably by cold sulphate waters, quartz is notably absent. The valuable contribution of Wright and Larsen[2] on the use of quartz as a geologic thermometer should be mentioned here, since it suggests methods that may lead to a more definite understanding of the genesis of quartzose deposits.

Chalcedony, chert, jasper, and like minerals are cryptocrystalline forms of silica that are deposited under different conditions of temperature and pressure. They are more abundant in deposits formed by sedimentary processes, in cold-water deposits, in secondary zones, in sinters, and in veins of late geologic age than in veins formed at great depth under higher temperature and pressure. In such veins

[1] Buckley, E. R., Geology of the disseminated lead deposits of St. Francois and Washington counties, Mo.: Missouri Bur. Geology and Mines, vol. 9, pt. 1, p. 249, 1909.

[2] Wright, F. E., and Larsen, E. S., Quartz as a geologic thermometer: Am. Jour. Sci., 4th ser., vol. 28, p. 421, 1909.

crystalline quartz is more common. Chalcedony, like quartz, may replace other minerals metasomatically. A. F. Rogers mentions an example of chalcedony from Guanajuato, Mexico, in the form of hollow, doubly terminated scalenohedrons after calcite.[1]

The association of sulphide ores with abundant quartz is commonly supposed to indicate that they were deposited by alkaline solutions. A study of the paragenesis of most deposits yields results that are in harmony with this conclusion, for quartz, as above stated, is deposited only sparingly with secondary sulphide ores. In some deposits, however, it occurs as veinlets and filling small cavities and is clearly more recent than the bulk of the ore. Some such veinlets are doubtless formed by deposition from descending solutions. At Tintic, Utah, where it lines druses in decomposed vein rock, evidence of deposition of quartz in late stages of ore formation is very clear.[2] At Lake City, Colo., according to Irving and Bancroft,[3] the white quartz occurs without question in more than one generation, but the bulk of it is younger than any of the metallic minerals, for it cuts through sphalerite, galena, tetrahedrite, pyrite, and rhodochrosite. Veinlets of this white quartz also commonly cement shattered masses of the metallic minerals.

Secondary polybasite and pyrargyrite are intergrown and apparently contemporaneous with quartz in secondary ore from the 300-foot level of the Big Seven mine, Neihart, Mont.[4] Quartz of very late age cuts turquoise in deposits near Tyrone, N. Mex.[5] At Cripple Creek[6] quartz replaces celestite, but the period of its genesis is uncertain. As emphasized by Van Hise,[7] the quartz deposited by descending waters is laid down mainly below the zone of weathering in the "belt of cementation." In some of the Lake Superior iron ores that have been altered by surface agencies it has been deposited in great quantities. Lindgren places it in the group with muscovite, epidote, pyrite, and other minerals that are formed distinctly below the zone of active oxidation.

The secondary chalcedonic quartz that is commonly associated with sulphide ores should be especially noted here. At Cananea, Mexico;

[1] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 18, 1910.

[2] Tower, G. W., and Smith, G. O., Geology and mining industry of the Tintic mining district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, pp. 692, 704, 1899.

[3] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, p. 60, 1911.

[4] Bastin, E. S., Metasomatism in downward sulphide enrichment: Econ. Geology, vol. 8, p. 59, 1913.

[5] Paige, Sidney, The origin of turquoise in the Burro Mountains, N. Mex.: Econ. Geology, vol. 7, p. 382, 1912.

[6] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 123, 1906.

[7] Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, pp. 634–636, 1904.

Morenci, Ariz.; Goldfield, Nev.; and near Silverton, Colo. (Yankee Girl and similar deposits), many of the ore deposits are capped with highly siliceous outcrops, whereas the ore at short distances below the surface is not so siliceous. A concentration of silica at the surface in some of these deposits is unmistakable, yet in several of them not all the silica appears to be residual quartz of the ore accumulated at the surface by the removal of other minerals. Some shallow pits at Cananea pass through a siliceous capping into white material, streaked with iron oxide, consisting principally of sericite and kaolin with small crystals of pyrite and chalcopyrite and probably of some residual feldspar. This loose cellular material contains very little free silica, and some of its pore spaces have forms of iron and copper sulphides. It is a natural inference that sulphate solutions have attacked the kaolin and by long-continued action have removed aluminum and set silica free. Analyses of mine waters indicate that some acid solutions dissolve aluminum in considerable quantities, for it is present in appreciable amounts in nearly all the waters and was noted in four samples from Cananea. (See p. 87.)

Kaolin is generally regarded as a comparatively stable mineral in the oxidized zone. At Morenci, Ariz., however, according to Lindgren,[1] kaolin is decomposed by acids, which carry aluminum into solution. Such reactions may be attended by the liberation of silica, which presumably would be hydrous silica, but at the very surface, perhaps, the hydrous varieties are dehydrated to form quartz, after the manner that limonite is dehydrated in hot dry climates to form hematite.

Siliceous cappings are extensively developed in and near the copper-bearing porphyry at Ely, Nev. Lawson[2] has shown, however, that some of the siliceous material or "blout" that outcrops at Ely is probably residual jasper.

The thin siliceous mantle above kaolinized, pyritized, sericitized feldspar at Cananea, Mexico, has already been mentioned. At Mount Morgan, Australia, large bodies of spongy siliceous ore are found above kaolin in the oxidized zone.[3]

In exploiting the bauxite deposits of Arkansas, I am informed by Mr. Julius Segall,[4] it is common practice to throw away about 2 feet of the surface mantle above the ore because it is too siliceous to be profitably treated.

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[1] Lindgren, Waldemar. The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 193, 1905.

[2] Lawson, A. C., The copper deposits of the Robinson mining district, Nevada: California Univ. Dept. Geology Bull., vol. 4, p. 327, 1906.

[3] Maclaren, Malcolm, Gold, p. 335, 1908.

[4] Oral communication.

SULPHUR AND SULPHATES.

PRINCIPAL MINERALS.

The chemical composition of the principal sulphates is shown below:

Anglesite	$PbSO_4$.
Leadhillite	$4PbO.SO_3.2CO_2.H_2O$.
Goslarite	$ZnSO_4.7H_2O$.
Pisanite	$(Cu,Fe)SO_4.7H_2O$.
Chalcanthite	$CuSO_4.5H_2O$.
Brochantite	$Cu_4SO_4(OH)_6$.
Plumbojarosite	$Pb[Fe(OH)_2]_6[SO_4]_4$.
Melanterite	$FeSO_4.7H_2O$.
Mallardite	$MnSO_4.7H_2O$.
Jarosite	$K_2O.3Fe_2O_3.4SO_3.6H_2O$.
Alunite	$K_2O.3Al_2O_3.4SO_3.6H_2O$.
Gypsum	$CaSO_4.2H_2O$.
Barite	$BaSO_4$.
Celestite	$SrSO_4$.
Anhydrite	$CaSO_4$.

The genesis of the principal sulphates of copper, lead, zinc, aluminum, and iron has already been considered. In all their occurrences in lode ores these minerals are probably secondary, except alunite, the sulphate of aluminum and potash, which is primary in some deposits. Several of the sulphates—for example, those of magnesium, manganese, zinc, and silver—are so soluble that they rarely accumulate in ore deposits and are of little or no importance as vein minerals.

SOLUBILITIES OF SULPHATES.

The solubilities of some of the sulphates (determined by Kohlrausch) are stated below:

K_2SO_4.	Na_2SO_4.	Ag_2SO_4.	$BaSO_4$.	$SrSO_4$.	$CaSO_4$.	$MgSO_4$.	$ZnSO_4$.	$PbSO_4$.
111.1 .62	168.3 1.15	5.5 .02	0.0023 .00001	0.11 .0006	2.0 .015	354.3 2.8	531.2 3.1	0.041 .00013

The upper number shows the number of grams in a solution of 1 liter of water; the lower number the molar solubility.

Of the sulphates that occur as gangue minerals, gypsum and barite are common. Anhydrite[1] is much less common, although it is abundant as a gangue mineral in some deposits of the Newhouse district, Utah. Under oxidizing conditions it is unstable and passes into the hydrated calcium sulphate, gypsum.

[1] Lindgren, Waldemar, Anhydrite as a gangue mineral: Econ. Geology, vol. 5, 1910, p. 525.

In lode deposits formed by ascending hot waters gypsum is secondary, except perhaps in some formed very near the surface; barite and celestite are both primary and secondary; anhydrite is primary.

OCCURRENCE OF SULPHUR AND SULPHATES.

Native sulphur is not an abundant alteration product of sulphide ores. The sulphur of commerce is obtained from other sources. Small quantities of sulphur, however, are not rare in oxidized or partly oxidized ores. Sulphur occurs in considerable quantities in the oxidized zone of the Horn Silver mine, Utah, and small crystals were found in ore from the Red Warrior mine, associated with cerusite.[1] Sulphur is found also in the Sunshine mine, a few miles south of Mercur, Utah,[2] with anglesite. Crystals of sulphur coat cavities in galena at Tintic, Utah.[3]

In the Mineral Hill district, Lemhi County, Idaho, as noted by Umpleby, a little sulphur fills small cavities from which pyrite had been dissolved.[4] According to Spurr, sulphur has formed on the outside of sulphide ore on the dump of the Leadville mine at Aspen.[5] It incrusts sulphide ores in the Bunker Hill mine at Henderson, Mont., and occurs very sparingly in the altered ores of Ducktown, Tenn. In a mine at Galena, Kans., according to Rogers,[6] sphalerite alters to sulphur. It is an alteration product of galena in the Mountain View lead mine of Carroll County, Md.,[7] and in the Wheatley mine, near Phoenixville, Pa.[8] Sulphur is associated with celestite in Monroe County, Mich.

As shown by Vogt, sulphur is formed by the reaction of several sulphides with ferric chloride. According to Stokes,[9] sulphur is formed in the first stage of the oxidation of pyrite. He writes the reaction:

$$FeS_2+Fe_2(SO_4)_3=3FeSO_4+2S.$$

The sulphur readily reacts with ferric sulphate to give more ferrous sulphate and acid:

$$2S+6Fe_2(SO_4)_3+8H_2O=12FeSO_4+8H_2SO_4.$$

[1] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 92, 1913.

[2] Spurr, J. E., Economic geology of the Mercur mining district, Utah: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 433, 1895.

[3] Tower, G. W., jr., and Smith, G. O., Geology and mining industry of Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 704, 1899.

[4] Umpleby, J. B., Geology and ore deposits of Lemhi County, Idaho: U. S. Geol. Survey Bull. 528, p. 79, 1913.

[5] Spurr, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, p. 239, 1898.

[6] Rogers, A. F., Am. Philos. Soc. Proc., vol. 49, p. 22, 1910.

[7] Williams, G. H., Zeitschr. Kryst. Min., vol. 22, p. 575, 1894.

[8] Hintze, Carl, Handbuch der Mineralogie, Band 1, p. 90.

[9] Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 15, 1901.

In the presence of ferrous sulphate and hydrogen sulphide sulphur unites with ferrous sulphide[1] to form pyrite, and it will unite with silver, mercury, and copper to form sulphides of those metals.

Gypsum, $CaSO_4.2H_2O$, is a common mineral of ore veins but is rare in parts of deposits that have not been exposed to oxidizing solutions. In all deposits formed by ascending hot waters it is probably secondary except near orifices of hot springs. It is generally formed through the agency of sulphuric acid or other soluble sulphates. According to A. E. H. Tutton,[2] gypsum is decomposed at 150° C. and possibly at 120° C. It has probably been formed invariably at low temperatures. Gypsum is present in decomposed vein matter at Cripple Creek[3] and at Creede, Colo., and in the secondary sulphide zone at Butte, Mont.[4] Veinlets of gypsum are abundant at Ely, Nev., in ores in porphyry. At Morenci, Ariz., according to Lindgren,[5] gypsum is present in oxidized deposits in limestone, where copper carbonates are formed by reaction between sulphates and calcium carbonates. It forms from calcite at Aspen, Colo.,[6] and is in part postglacial, for it cements glacial débris. It is associated with the altered ores at Tonopah, Nev.,[7] and is present in most of the deposits of Goldfield, Nev.,[8] where it occurs below the zone of oxidation. In the Dixon mine, Bingham, Utah, according to Boutwell,[9] a considerable body of gypsum was found between the carbonate lead-silver ore and the parent sulphides. Crystals of gypsum are coated with hematite in the Ajax mine at Tintic, Utah.[10]

Gypsum is abundant in the Cactus mine, San Francisco region, Utah, where, as noted below, anhydrite alters to gypsum. It is formed in this region also as a decomposition product of other minerals and it occurs in fissures in limestone, where sulphuric acid has reacted on the calcium carbonate. It is now being deposited from spring waters south of the Frisco Contact mine.[11] At Park

[1] Allen, E. T., Crenshaw, J. L., and Johnston, John, The mineral sulphides of iron: Am. Jour. Sci., 4th ser., vol. 33, p. 169, 1912.

[2] Tutton, A. E. H., The optical constants of gypsum at different temperatures: Roy. Soc. London Proc., vol. 81A, p. 40, 1908. See also Melcher, A. C., Am. Chem. Soc. Jour., vol. 32, p. 50, 1910.

[3] Lindgren, Waldemar, and Ransome, F. L., Geology and ore deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 125, 1906.

[4] Winchell, A. N., Discussion of paper by F. L. Ransome on Criteria of downward sulphide enrichment: Econ. Geology, vol. 5, p. 489, 1910.

[5] Lindgren, Waldemar, The copper deposits of the Clifton-Morenci district, Arizona: U. S. Geol. Survey Prof. Paper 43, p. 120, 1905.

[6] Spurr, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, p. 24, 1898.

[7] Spurr, J. E., Geology of the Tonopah mining district, Nevada: U. S. Geol. Survey Prof. Paper 42, p. 96, 1905.

[8] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 128, 1909.

[9] Boutwell, J. M., Economic geology of the Bingham mining district, Utah: U. S. Geol. Survey Prof. Paper 38, pp. 119, 204, 1905.

[10] Tower, G. W., jr., and Smith, G. O., Geology and mining industry of the Tintic district, Utah: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 3, p. 694, 1899.

[11] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 108, 1913.

City, Utah,[1] gypsum has apparently been deposited from mine waters on an old dump in Thaynes Canyon, and it forms crusts on mine workings and old dumps at Butte.[2]

Barite, $BaSO_4$, has not been identified in igneous rocks, in pegmatites, or in contact-metamorphic ores but is found in both the oxidized and unoxidized portions of ore lodes. It is not unknown in some deposits presumably formed at considerable depths. In the Gold Hunter mine of the Coeur d'Alene district[3] it is associated with galena, sphalerite, and tetrahedrite. In this district it is present also in the ore of the Standard-Mammoth mine. In some of the sulphide copper ores of Shasta County, Cal.,[4] barite is a characteristic gangue mineral. In many deposits of later age, which were presumably formed nearer the surface, barite is abundant. It is present in many lode deposits of southwestern Colorado, in some of which, as noted by Irving and Bancroft,[5] it was formed by ascending hot waters. In some veins that are of great vertical extent barite is abundant in their higher portions but absent at greater depths. It is inferred that the barite is primary but was deposited under lower temperatures than those which prevailed in the deeper parts of the veins. In many Lake City deposits it is the most abundant mineral. It is clearly of earlier deposition than quartz, for quartz very commonly incrusts crystals of barite that project into central cavities.

The deposits at Creede, Colo.,[6] contain considerable barite. Some of the barite has formed as a primary constituent of the ore, but some that fills cracks and crevices in limonite is later than the first period of mineralization and is probably secondary. At Wagon-wheel Gap, near by, it has formed along a fissure near which hot springs now issue.[7] At Aspen, Colo., barite is cut by veinlets of argentite and native silver and is intimately associated with polybasite.[8] It is found with kaolinite in deposits at Goldfield, Nev.[9]

[1] Boutwell, J. M., Geology and ore deposits of the Park City district, Utah: U. S. Geol. Survey Prof. Paper 77, p. 115, 1912.

[2] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 83, 1912.

[3] Ransome, F. L., and Calkins, F. C., The geology and ore deposits of the Coeur d'Alene district, Idaho: U. S. Geol. Survey Prof. Paper 62, p. 103, 1908.

[4] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 102, 1910.

[5] Irving, J. D., and Bancroft, Howland, Geology and ore deposits near Lake City, Colo.: U. S. Geol. Survey Bull. 478, pp. 34, 35, 45, 1911.

[6] Emmons, W. H., and Larsen, E. S., Geology and ore deposits of Creede, Colo.: U. S. Geol. Survey Bull. — (in preparation).

[7] Emmons, W. H., and Larsen E. S., The hot springs and mineral deposits of Wagon-wheel Gap, Colo.: Econ. Geology, vol. 8, p. 241, 1913.

[8] Spurr, J. E., Geology of the Aspen mining district, Colorado: U. S. Geol. Survey Mon. 31, p. 228, 1898.

[9] Ransome, F. L., The geology and ore deposits of Goldfield, Nev.: U. S. Geol. Survey Prof. Paper 66, p. 127, 1909.

Although barite is a characteristic mineral of the cobalt-silver ores of the Erzgebirge, it has not been recognized in the Cobalt[1] district, Ontario. It is present, however, according to Miller, in the cobalt-silver ores at Port Arthur, at Elk Lake and in some other silver-bearing districts in Ontario.

Barite is commonly present in the gangue of copper deposits in the "Red Beds"[2] of the Southwest that have been formed through the agency of cold solutions.

In the New Brancepeth colliery, near Durham, England, a large barite vein occupies a fault fissure in Carboniferous rocks. The barite is associated with subordinate sulphides. To 1908 this deposit had yielded about 30,000 tons of barite.[3] The deposit was easily permeable to cold solutions. The waters of collieries of Durham and Northumberland carry barium, and the pipes[4] that lead waters from the coal pits contain barium sulphate. In the mine the barite alters to witherite, which is coated with alstonite $(Ba,Ca)CO_3$. Crystals of barite have been found in cavities of Northumberland witherite.[5]

Although barite forms near the surface, it is not so commonly associated with the secondary sulphides as gypsum and kaolin. Owing to its insolubility, it persists in the oxidized zones. In many deposits it outcrops at the surface, and it is found in oxidized ores from which all the sulphides have been dissolved. Undoubtedly barite can replace limestone in cold solutions. A. F. Rogers[6] mentions an example of *Productus* and other calcareous shells at Elmont, Kans., in various states of replacement by barite. At Batson and Saratoga, Tex.,[7] pisolitic and oolitic barite was found in drill holes at depths of 1,000 feet or more—an unusual occurrence. As the barite is associated with warm acid water and oil, and as a sandstone is mammillated on the lower side, Moore suggests that the barium was carried upward by ascending hot water as bicarbonate or in alkali carbonate solutions and precipitated on coming in contact with acid.

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[1] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming: Ontario Bur. Mines Rept., vol. 19, pt. 2, pp. 12, 28, 1913.

[2] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 78, 1910.

[3] Peel, R., Notes upon an occurrence of barytes in a 20-fathom fault at New Brancepeth colliery: Colliery Manager and Jour. Min. Eng., vol. 16, pp. 56–58, London, 1900.

[4] Clowes, F., Deposits of barium sulphate from mine waters: Roy. Soc. London Proc., vol. 44, p. 368, 1889.

[5] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 22, 1910.

[6] Idem, p. 21.

[7] Moore, E. S., Oolitic and pisolitic barite from the Saratoga oil field, Texas: Geol. Soc. America Bull., vol. 25, p. 77, 1914.

At Doughty Springs, Colo.,[1] in which sodium, chlorine, hydrogen sulphide, and carbon dioxide are abundant, the latter both as gas and as bicarbonates, much barite sinter is being deposited to-day. Whether the barium is carried as a bicarbonate, as sulphate, dissolved in alkali carbonate, or as silicate, it would be precipitated by sulphuric acid or by alkali sulphate.

Barium might be carried in hot solutions as the sulphate. Unlike gypsum (see p. 491), the solubility of barite is increased with increase of temperature.

Celestite, $SrSO_4$, is not known as an original constituent of igneous rocks, of pegmatites, or of contact-metamorphic deposits. It occurs in certain ore bodies that were formed relatively near the surface by hot ascending waters. It is formed also in deposits far removed from igneous rocks, and in some lodes it is probably a secondary mineral deposited by cold sulphate waters. It is not nearly so common as barite.

Although celestite is relatively rare in ore veins, at Cripple Creek it is both a primary and secondary mineral. Pseudomorphs of quartz after celestite are of common occurrence in some of the Cripple Creek deposits, and slender needles of celestite coat openings in the vein fissures far below the zones of oxidation.[2] In the Cresson ore body at Cripple Creek much celestite is present as gangue.

Although celestite is not a common gangue mineral in ore veins, it is found in considerable abundance in some beds of limestone. It is found in Strontium Cave, in the Monroe formation of Put-in-Bay Island, Lake Erie,[3] and in the limestones and shales of the Salina formation near Syracuse, N. Y.[4] In the Put-in-Bay region the celestite is disseminated in the limestone, and in the upper parts has been leached out, as is shown by cavities that remain. It is segregated here and there in crevices and cavities in the rocks. Strontium Cave, which is about 25 feet long, is lined with tons of large crystals that have been deposited by cold solutions. Although celestite is not highly soluble in acids, it is fairly soluble in water. At 15° C. 1 part dissolves in 10,101 parts of water;[5] calcite is soluble, 1 part in 76,924 parts of water.[5] The celestite disseminated in rocks near the surface would, by leaching, pass into solution, and as the solution descends the sulphate, by drying in air, may be again deposited in caverns and crevices.[6]

[1] Headden, W. P., The Doughty Springs, a group of radium-bearing springs, Delta County, Colo.: Am. Jour. Sci., 4th ser., vol. 19, p. 297, 1905.

[2] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 125, 1906.

[3] Kraus, E. H., Occurrence and distribution of celestite-bearing rocks: Am. Jour. Sci., 4th ser., vol. 19, p. 286, 1905.

[4] Kraus, E. H., Am. Jour. Sci., 4th ser., vol. 18, p. 30, 1904.

[5] Kraus, E. H., Occurrence and distribution of celestite-bearing rocks: Am. Jour. Sci., 4th ser., vol. 19, p. 289, 1905.

In Exeter Township, between Maybee and Scofield, Monroe County, Mich., celestite-bearing rocks carry also a considerable quantity of native sulphur.[1]

Celestite and fluorite have been noted also among minerals from quarries at Tiffin, Ohio, where they are found in the Monroe formation with calcite and sphalerite.[2] Crystals of celestite are found also near Austin, Tex. In this region cavities in massive celestite are lined with small crystals of strontianite.[3]

Anhydrite, $CaSO_4$, is an abundant constituent of certain beds of rock salt, where it is commonly associated with gypsum, with which it has formed contemporaneously. It is not a common gangue mineral in sulphide ore deposits but has been found at the Cactus mine, Beaver County, Utah,[4] where it is intergrown with chalcopyrite, tourmaline, and siderite. In the Little Neck vein, White Oaks district, New Mexico,[5] small veins, with tourmaline and gypsum, are found, the gypsum having probably been formed by the hydration of anhydrite. Bodies of gypsum, with pyrite and chalcopyrite, are found in the Bully Hill and Rising Star mines, Shasta County, Cal. Microscopic study shows that the gypsum contains cores of anhydrite, which is doubtless the parent mineral.[6]

According to Butler, the anhydrite in the Cactus mine, San Francisco district, Utah, alters extensively to gypsum near the surface. In this district gypsum occurs in considerable quantities, particularly in the upper levels of the mine. Some of it, on microscopic examination, was seen to contain cores of anhydrite. Butler states that material thrown on the dump only a few years ago is already largely altered to gypsum.[7]

Anhydrite is found in copper deposits of Cuka-Dulkan at Bor, East Serbia, where it is classed by Lazarevic[8] with secondary minerals. In view of its instability in cold surface waters, the validity of this conclusion is doubtful.

Near the Ludwig mine, Lyon County, Nev., a bed of calcium sulphate, which is 450 feet wide on the outcrop, is interstratified with

[1] Sherzer, W. H., Geology of Monroe County: Michigan Geol. Survey, vol. 7, pt. 1, pp. 208, 212, 1900.

[2] Hobbs, W. H., Contributions from the mineralogical laboratory of the University of Wisconsin: Am. Geologist, vol. 36, p. 181, 1905.

[3] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 22, 1910.

[4] Lindgren, Waldemar, Anhydrite as a gangue mineral: Econ. Geology, vol. 6, p. 522, 1910.

[5] Lindgren, Waldemar, Graton, L. C., and Gordon, C. H., The ore deposits of New Mexico: U. S. Geol. Survey Prof. Paper 68, p. 181, 1910.

[6] Graton, L. C., The occurrence of copper in Shasta County, Cal.: U. S. Geol. Survey Bull. 430, p. 100, 1910.

[7] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 106, 1913.

[8] Lazarevic, M., Die Enargit-Covellin-Lagerstätte von Cuka-Dulkan bei Bor in Ost-Serbien: Zeitschr. prakt. Geologie, vol. 20, p. 337, 1912.

limestone and quartzite and extends along the strike 4,000 feet. At the surface the bed is pure white gypsum, but at a depth of about 400 feet gypsum gives way to anhydrite. Specimens of gypsum contain cores of unaltered anhydrite. Rogers[1] concludes that the anhydrite is of sedimentary origin and that the gypsum is secondary after anhydrite.

As shown by Melcher,[2] calcium sulphate is almost insoluble at temperatures around 218° C., and as pointed out by Lindgren,[3] it could be precipitated at high temperatures. Both gypsum and anhydrite show decreasing solubility in water above about 40° C. Anhydrite is stable, however, at higher temperatures than gypsum.

CARBONATES.

The principal carbonates are listed below:

Calcite.....$CaCO_3$.
Aragonite.....$CaCO_3$.
Dolomite.....$(Ca,Mg)CO_3$.
Magnesite.....$MgCO_3$.
Siderite.....$FeCO_3$.
Ankerite.....$(Ca,Mg,Fe)CO_3$.
Oligonite.....$(Fe,Mn)CO_3$.
Rhodochrosite.....$MnCO_3$.
Manganosiderite.....$(Mn,Fe)CO_3$.
Manganocalcite.....$(Mn,Ca)CO_3$.
Witherite.....$BaCO_3$.
Strontianite.....$SrCO_3$.
Smithsonite.....$ZnCO_3$.
Monheimite.....$(Zn,Fe)CO_3$.
Cerusite.....$PbCO_3$.
Sphærocobaltite.....$CoCO_3$.
Malachite.....$CuCO_3.Cu(OH)_2$.
Azurite.....$2CuCO_3.Cu(OH)_2$.
Bismutite.....$Bi_2O_3.CO_2.H_2O$.
Aurichalcite.....$2(Zn,Cu)CO_3.3(Zn,Cu)(OH)_2$.
Hydrozincite.....$ZnCO_3.2Zn(OH)_2$.

Solubilities of some carbonates in water at 18°.

K_2CO_3.	Na_2CO_3.	Ag_2CO_3.	$BaCO_3$.	$SrCO_3$.	$CaCO_3$.	$MgCO_3$.	$ZnCO_3$.	$PbCO_3$.
1,080 5.9	193.9 1.8	0.03 .0001	0.023 .00011	0.011 .00007	0.013 .00013	1.0 .01	0.04? .0003?	0.001 .00003

The upper number gives the grams of anhydrous salt held in solution by 1 liter of water; the lower number the molar solubility or number of mols contained in a liter of the saturated solution. The

[1] Rogers, A. F., The occurrence and origin of gypsum and anhydrite at the Ludwig mine, Lyon County, Nev.: Econ. Geology, vol. 7, p. 188, 1912.

[2] Melcher, A. C., The solubility of silver chloride, barium sulphate, and calcium sulphate at high temperatures: Am. Chem. Soc. Jour., vol. 32, pp. 50–66, 1910.

[3] Lindgren, Waldemar, op. cit., p. 527.

determinations were made by Kohlrausch by the conductivity method.

The principal carbonate ores, those of iron, copper, lead, zinc, manganese, and other metals have been discussed in the sections of this paper devoted to those metals. The alkali carbonates are so soluble that they rarely form except in arid countries by evaporation. The alkaline earth carbonates are of interest chiefly as gangue minerals. Of these calcite, aragonite, and dolomite are common; witherite and strontianite are comparatively rare, and are chiefly secondary after barite and celestite. Magnesium carbonate is formed extensively by the surface alteration of igneous rocks, particularly in cracks traversing serpentine. Because the carbonates of copper, lead, and zinc are so insoluble in acid they form extensively in oxidizing zones. None of these carbonates form in depth from hot solutions. Carbonates of calcium, magnesium, iron, and manganese rarely form in the gossans of pyritic ore because they are soluble in acid waters, but at depths where solutions become very feebly acid, neutral, or alkaline, they may be deposited. Zinc carbonate is formed near the surface, especially in lodes in limestone. Siderite, ferrous carbonate, is less common in the lode deposits than calcite, dolomite, or rhodochrosite. It is generally primary. It is deposited, however, under some conditions of sedimentation—for example, in the "black band" iron ores. Its occurrence as a product of surface alteration is exceedingly rare, although the ferrous carbonate molecule is present in ankerite and in some other carbonates which are assumed to be secondary in some deposits. According to Ransome,[1] impure siderite occurs in veinlets traversing sulphide ores at Breckenridge, Colo.

Rhodochrosite, the carbonate of manganese, is fairly abundant in many precious-metal ores. In the United States it is almost unknown in such deposits that are older than the Tertiary. There is little evidence that rhodochrosite is deposited by descending sulphate waters, although the manganese carbonate molecule is probably present in some complex carbonates that are believed to be secondary. In the bog manganese deposits, which have formed by sedimentary processes, the manganese oxides predominate, but some of these deposits contain also rhodochrosite.[2] Although the soluble carbonates precipitate silver carbonate from solutions of silver salts in the laboratory, and although silver sulphate is more soluble than silver carbonate, the latter is nevertheless unknown in mineral deposits.

[1] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 169, 1911.

[2] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geology, vol. 2, p. 306, 1894.

Calcite, $CaCO_3$, is an uncommon constituent of pegmatite veins and is exceedingly rare in igneous rocks.[1] When found in igneous rocks it is generally considered secondary, but under sufficient pressure, in places where carbon dioxide can not escape, it may form at high temperatures, and it is a common and abundant constituent of contact-metamorphic deposits. It is found also in deep veins and more abundantly as a gangue mineral in ores formed at moderate depths. It is also a product of hydrothermal alteration in the wall rocks of lodes at all depths but is most common in wall rocks of lodes formed relatively near the surface. Some of the great mineralized porphyries, such as those at Cananea, Mexico, and Morenci, Ariz., contain no primary calcite. The sericitized porphyry of Cananea, through hundreds of feet of drifts, does not effervesce at all in strong acid. In many other deposits, however, calcite has been formed at moderate depths by ascending hot waters, and it is formed abundantly also by cold waters. It is one of the most abundant gangue minerals in the lead and zinc ores of the Mississippi Valley, and it constitutes nearly all the gangue in the ore deposits of southwestern Wisconsin and northwestern Illinois. It is a common secondary mineral, deposited abundantly in zones above ground-water level where drippings from roofs of cavities form stalactites, stalagmites, organ pipes, and like features of caverns. It is generally leached entirely from a thoroughly decomposed gossan of iron sulphide lodes, and is deposited at great depths in such lodes where openings are available, its secondary crystals commonly lining vugs. Calcite is secondary in the San Francisco region, Utah,[2] in the Little Mina workings at Butte,[3] and in many other deposits of the western United States. There is very little calcite in most of the veins of Butte, however, or in the silver lodes of Philipsburg, Mont.[4] Near Joplin, Mo., huge scalenohedral crystals several feet long form near the surface.[5]

Calcium carbonate is one of the most mobile of natural substances in its geologic activities. It is dissolved sparingly in pure water and very readily in water that carries only a little carbon dioxide. It is dissolved also in very dilute sulphuric acid, hydrochloric acid, and in other acids. In the oxidizing zone dripping water will slowly evaporate, and if it contains much carbon dioxide some of it will escape. Either evaporation or loss of carbon dioxide will

[1] Adams, F. D., On the occurrence of a large area of nepheline syenite in the township of Dungannon, Ontario: Am. Jour. Sci., 3d ser., vol. 48, p. 14, 1894.

[2] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 99, 1913.

[3] Weed, W. H., Geology and ore deposits of the Butte district, Montana: U. S. Geol. Survey Prof. Paper 74, p. 83, 1912.

[4] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 157, 1913.

[5] Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 13, 1907 (reprinted, 1914).

cause precipitation of calcium carbonate. Natural conditions near the border line between those that favor solution and those that favor the precipitation of calcite appear to be common in nature, particularly near the surface. Since acid drives out carbon dioxide from calcite with effervescence, calcite can not form in a highly acid environment, but it might form in very faintly acid solutions. It is commonly intergrown with marcasite and is associated with metacinnabarite. According to Allen and Crenshaw,[1] these sulphides form only in acid solutions. In pyritic lodes that are undergoing superficial decomposition, secondary calcite and dolomite are more abundant in the lower part of the zone of alteration than in the upper part. Secondary calcite is not rare in the lower part of some secondary sulphide zones. Secondary chalcocite from Mount Morgan, Queensland, incloses numerous minute crystals of calcite. Calcite is both primary and secondary in a large number of gold deposits and silver deposits in the western Cordilleras.

Calcium carbonate is rarely pure, for it generally contains magnesium, iron, or manganese. The calcite from a quarry near Eskifjördhr, on the east coast of Iceland, is well known for its purity. The country is a plateau formed of volcanic rocks that are deeply entrenched by fjords, and the quarry is on land that slopes about 40°. It is in dolerite, and the opening, according to J. L. Hoskyns-Abrahall,[2] is about 25 by 60 feet and 10 feet high. It was filled with closely fitting crystals 10 inches across that formed a compact mass. Minute crystals of stilbite cover surfaces of the calcite. The surrounding dolerite is traversed by small veinlets or ramifications of calcite which lead to the deposit. The waters now in the calcite body are not capable of depositing calcite, but, according to Hoskyns-Abrahall, they etch the mineral.

Aragonite, $CaCO_3$, is orthorhombic, whereas calcite is rhombohedral. Aragonite often forms radiating groups of acicular crystals or fibrous nodules and crusts. It is very common in beds of gypsum and it occurs in some sedimentary iron ores and other sediments. It is commonly associated with gypsum. Its geologic range is smaller than that of calcite; it probably does not form at high temperatures except very near the surface, where pressures are low, and at orifices of hot springs. Aragonite is commonly formed as a secondary mineral in lode ores and is common in cavities in limestone, where it forms roofs and floors. Its growth may be rapid. Curtis[3] mentions aragonite crystals in a mine in the Eureka district,

[1] Allen, E. T., and Crenshaw, J. L., The sulphides of zinc, cadmium, and mercury; their crystalline forms and genetic conditions: Am. Jour. Sci., 4th ser., vol. 34, pp. 341–396, 1912.

[2] Hoskyns-Abrahall, J. L., A visit to the calcite quarry in Iceland: Mineralog. Mag., vol. 9, p. 179, 1892.

[3] Curtis, J. S., Silver-lead deposits of Eureka, Nev.: U. S. Geol. Survey Mon. 7, pp. 56–57, 1884.

Nevada, which were forming in dripping water. Observations made from time to time by means of a transit placed on a permanently fixed tripod showed that the crystals that were forming in a moist drip grew rapidly, one growing five-sixteenths of an inch in three weeks. During the first part of that time the crystal formed most rapidly and seemed to shoot out of a drop of water. Its increase was then perceptible from day to day. The growth of this crystal, as well as others in the group, was evidently dependent on the size of the surrounding drip of water, for although the whole group of crystals was wet, increase was perceptible only in crystals surrounded by drops of water.

Dolomite, $(Ca,Mg)CO_3$, is a common mineral in ore deposits, though less common than calcite. "Normal" dolomite ($CaCO_3$. $MgCO_3$) contains a molecule each of calcium carbonate and magnesium carbonate, but a great many specimens do not show this ideal proportion. Dolomite is unknown as a primary igneous or rock-making mineral; it occurs, though rarely, in pegmatites and is found in lode ores formed under all conditions. It is therefore one of the persistent minerals in ore deposits, in which it has essentially the same chemical range as calcite.

It is common in the zinc and lead deposits of the Mississippi Valley but more abundant in the ores of many camps in the Joplin region than in the ores of southwestern Wisconsin and Illinois.[1] Fine saddle-shaped crystals are found in the Joplin region, where the country rock is limestone and the ore deposits carry much dolomite. The ores in southwestern Wisconsin, where the country rock is dolomite, carry much calcite and little dolomite.[2] In gold and silver lodes of the American Cordilleras little rhombohedrons of dolomite commonly line vugs in the zone of sulphide enrichment. It is secondary in some mines of the San Francisco region, Utah,[3] at Philipsburg, Mont.,[4] and in several other districts. At Cobalt, Ontario,[5] according to Miller, calcite, the white carbonate, is the most characteristic of the veins that carry good ore; a pink carbonate (dolomite) comes in at greater depths and is frequently found at places where deposits are becoming less valuable. This relation, however, does not hold invariably in this district.

Magnesite, $MgCO_3$, the pure mineral, is comparatively rare. It is not known as a constituent of pegmatites, of contact-metamorphic

[1] Bain, H. F., Lead and zinc deposits of the upper Mississippi Valley: U. S. Geol. Survey Bull. 294, p. 51, 1906. Siebenthal, C. E., U. S. Geol. Survey Geol. Atlas, Joplin district folio (No. 148), p. 13, 1907 (reprinted, 1914).

[2] Bain, H. F., op. cit., p. 51.

[3] Butler, B. S., Geology and ore deposits of the San Francisco and adjacent districts, Utah: U. S. Geol. Survey Prof. Paper 80, p. 99, 1913.

[4] Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg quadrangle, Montana: U. S. Geol. Survey Prof. Paper 78, p. 157, 1913.

[5] Miller, W. G., The cobalt-nickel arsenides and silver deposits of Temiskaming (4th ed.): Ontario Bur. Mines Rept., vol. 19, pt. 2, p. 28, 1913.

deposits, or of lodes formed at great depth. It occurs, however, in some vein deposits formed near the surface and is a product of decomposition of olivine and other magnesian minerals. The reaction converting olivine to serpentine, magnetite, and magnesite may be represented as follows:[1]

$$3Mg_3FeSi_2O_8+3H_2CO_3+H_2O+O= 2H_4Mg_3Si_2O_9+Fe_3O_4+3MgCO_3+2SiO_2.$$

A reaction with iron-bearing olivine which does not form magnetite is also possible:

$$Mg_3FeSi_2O_8+2H_2CO_3+H_2O=\underset{\text{Serpentine.}}{H_4Mg_3Si_2O_9}+FeH_2(CO_3)_2.$$

Also another, with iron-free olivine:

$$2Mg_2SiO_4+H_2CO_3+H_2O=H_4Mg_3Si_2O_9+MgCO_3.$$

In the serpentine areas of California[2] magnesite veins are very numerous. In secondary zones of sulphide ores pure magnesite is very rare. Mineral waters generally carry calcium and iron as well as magnesium, and the carbonates precipitated from them are generally combinations of the carbonate molecules such as ankerite and dolomite.

Siderite is discussed on page 454.

Ankerite is "normally" $2CaCO_3.MgCO_3.FeCO_3$, but the amounts of each carbonate molecule vary and the more nearly representative formula is $CaCO_3(Mg,Fe,Mn)CO_3$. The crystals resemble calcite in form, and some are white or gray with red tints where manganese increases. There are all combinations of these carbonate molecules—siderite, rhodochrosite, dolomite, and calcite. Frequently, when the four metals can be detected qualitatively, the mineral has been termed ankerite without further analysis. Ankerite has in veins the same geologic range as calcite. It is both a primary and a secondary mineral, and, like calcite, is formed at depths in secondary sulphide zones, where it commonly lines vugs. In the Georgetown region, Colo.,[3] it is both primary and secondary. In the Breckenridge district, Colo.,[4] it lines vugs and cracks in sulphide ores and forms rhombohedrons and botryoidal incrustations on sphalerite and other sulphides. With siderite ankerite forms in bog ores of iron and manganese, and with iron carbonate it is present in sedimentary iron formations.

Rhodochrosite and other manganiferous carbonates are discussed on page 443.

[1] Van Hise, C. R., A treatise on metamorphism: U. S. Geol. Survey Mon. 47, p. 309, 1904.
[2] Hess, F. L., The magnesite deposits of California: U. S. Geol. Survey Bull. 355, 1908.
[3] Spurr, J. E., Garrey, G. H., and Ball, S. H., Economic geology of the Georgetown quadrangle, Colorado: U. S. Geol. Survey Prof. Paper 63, p. 259, 1908.
[4] Ransome, F. L., Geology and ore deposits of the Breckenridge district, Colorado: U. S. Geol. Survey Prof. Paper 75, p. 87, 1911.

Witherite, $BaCO_3$, is a secondary mineral formed by decomposition of barite, and possibly of other minerals. It is unknown as a primary mineral in lode ores of the United States. It occurs in considerable abundance at Fallowfield, near Hexham, in Northumberland, England, and at New Brancepeth colliery, near Durham, 30 miles southeast of Fallowfield. This colliery had produced about 30,000 tons of barite to 1908. The ores are found in a fault fissure[1] that cuts Carboniferous sandstones, shales, limestones, and coal. In this region sideritic deposits also are found in several other fissures in the coal series.[2] The deposits of this region are apparently of somewhat similar genesis to those of the Joplin region. The Fallowfield mine was once worked for galena. The Brownley Hill mine, near Alston, Cumberland, is worked for zinc. The New Brancepeth vein carries only a little galena and sphalerite and is worked for barite. According to Spencer,[3] the barite and witherite of this deposit are in a sandstone breccia that contains fragments of coal. The barite is corroded and nearly all of it is older than witherite, the latter having probably formed by carbonated waters reacting on barite. The witherite is in turn capped with alstonite $(Ba,Ca)CO_3$. Generally the witherite occurs as small buttons, nodules, or crusts on the barite. Besides the sphalerite and galena, a little pyrite and chalcopyrite are associated with these ores, and in rare occurrences[4] barite appears to be later than the carbonate.[5] Some barium is carried by the mine waters of this region,[6] and barium sulphate is now being deposited in pipes. Here also a very insoluble mineral, barite, has altered to one that is much more soluble, witherite. This alteration could take place only with a fairly high concentration of carbonate and with little sulphuric acid in solution. Barite veins with much pyrite are very numerous in the western United States, but witherite is practically unknown in them. It has been reported, however, from baritic deposits near Lexington, Ky., and it has been found in a silver-bearing vein near Thunder Bay, Lake Superior.

Strontianite, $SrCO_3$, is not an abundant gangue mineral in ore lodes. It is found in some limestone beds and is commonly asso-

[1] Peel, R., Notes on the occurrence of barite in a 20-fathom fault at New Brancepeth colliery: The Colliery Manager and Journal of Engineering, vol. 16, p. 56, London, 1900. Lebour, G. A., Discussion of paper above cited: Idem, p. 58.

[2] Louis, Henry, Note on a mineral vein in Wearmouth colliery: Inst. Min. Eng. Trans. (England), vol. 22, p. 127, 1902.

[3] Spencer, L. J., On the occurrence of alstonite and ullmannite (a species new to Britain) in a barytes-witherite vein at the New Brancepeth colliery, near Durham: Mineralog. Mag., vol. 15, p. 302, 1910.

[4] Idem, p. 310.

[5] Rogers, A. F., Notes on some pseudomorphs, petrifactions, and alterations: Am. Philos. Soc. Proc., vol. 49, p. 21, 1910.

[6] Clowes, F., Deposits of barium sulphate from mine waters: Roy. Soc. London Proc., vol. 44, p. 360, 1889.

ciated with celestite.[1] Such is its occurrence near Schoharie, N. Y. Strontianite is associated with celestite in geodes in limestone at Clinton, N. Y.;[2] the carbonate incloses the sulphate and forms a white coating on surfaces of celestite crystals. Near Austin, Tex., strontianite is found in limestone associated with celestite, aragonite, and calcite. It is found in a vein with barite on Mainland, Orkney Islands,[3] and at Strontian, Argyllshire.[4]

Carbonates of lead, zinc, copper, and other metals are discussed with ores of those metals.

PHOSPHATES.

Pyromorphite	$Pb_5P_3O_{12}Cl$.
Hopeite	$Zn_3P_2O_8.H_2O$.
Vivianite	$Fe_3P_2O_8.8H_2O$.
Libethenite	$Cu_2(OH).PO_4$.
Turquoise	$CuO_2.Al_2O_3.2P_2O_5.9H_2O$.
Hinsdalite	$2PbO.3Al_2O_3.2SO_3.P_2O_5.6H_2O$.
Wavellite[5]	$4AlPO_4.2Al(OH)_3.9H_2O$.
Apatite	$CaClCa_4(PO_4)_3$.
Monazite	$(Ce,La,Di)PO_4$.
Xenotime	$YtPO_4$.
Triphylite	$Li(Fe,Mn)PO_4$.
Amblygonite	$AlPO_4.LiF$.

Phosphorus is a widely distributed constituent of the earth's crust and, according to Clarke,[6] constitutes 0.11 per cent of known terrestrial matter. The principal primary source is apatite, a mineral that occurs sparingly in nearly all igneous rocks. Many other primary minerals contain phosphorus, among them monazite, xenotime, triphylite, and amblygonite. Wavellite is both primary and secondary. Hinsdalite may be primary also in deposits formed near the surface, but its genesis is uncertain. Hopeite, pyromorphite, libethenite, and turquoise are all secondary. Vivianite is secondary also, but in some bog iron ores it is primary.

It is noteworthy that no phosphorus mineral has been identified in the great iron deposits of the Mesabi and Gogebic ranges of the Lake Superior region,[7] though many of the ores contain phosphorus in quantities sufficient to penalize their sale. The secondary phos-

[1] Phalen, W. C., Celestite deposits of California and Oregon: U. S. Geol. Survey Bull. 540, p. 524, 1914.

[2] Root, O., On a locality of carbonate of strontium: Am. Jour. Sci., 2d ser., vol. 13, p. 264, 1852.

[3] Heddle, M. F., The geognosy and mineralogy of Scotland: Mineralog. Mag., vol. 3, p. 224, 1880.

[4] Macadam, W. I., Analysis of a sample of strontianite from Strontian, Argyllshire: Mineralog. Mag., vol. 6, p. 173, 1885.

[5] Or $3Al_2O_3.2P_2O_5.12H_2O$.

[6] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 34, 1916.

[7] Van Hise, C. R., and Leith, C. K., Geology of the Lake Superior region: U. S. Geol. Survey Mon. 52, p. 248, 1911.

phates of lead and zinc are discussed in the matter devoted to the ores of those metals.

The sources of the phosphorus are not always clear. Some of it is probably derived from the breaking down of primary phosphates, particularly apatite, but some is doubtless introduced by organic agencies. The gossans of sulphide ores are likely to be loose and cavernous, and the caverns in many of them are inhabited by insects and small mammals, particularly bats and mountain rats. The waste and bodies of these animals may supply important contributions of phosphorus to underground waters. In this connection the hopeite and pyromorphite ores of Broken Hill, Rhodesia (see p. 379), are noteworthy. There phosphorus-bearing minerals, associated with galena and sphalerite, are found in large quantities, in part replacing bones in a cave that was occupied by early man.

Vivianite, $Fe_3P_2O_8.8H_2O$, is a common secondary mineral in clays and is found also in bog iron ores. Roots of a coniferous tree replaced by vivianite are found at a depth of 32 feet in a deposit of clay near Eddyville, Ky.[1]

Wavellite, $4AlPO_4.2Al(OH)_3.9H_2O$, is both a primary and secondary mineral in lode ores. Small masses of radiating crystals were noted by Penrose[2] in deposits of Cripple Creek. According to Lindgren and Ransome[3] it is a primary mineral associated with adularia in the Findlay mine. It is reported also in St. Clair County, Ala., 5 miles northeast of Coal City.[4] It has been mined for phosphorus near Mount Holly Springs, Pa. There, as stated by Stose,[5] it forms nodules and masses in white clay in surface sands with ores of manganese and limonite, and it is probably a disintegration product of older phosphatic beds.

Apatite (chlor-apatite, $(CaCl)Ca_4(PO_4)_3$; fluor-apatite, $(CaF)Ca_4(PO_4)_3$) is a persistent mineral, or one that is formed under a great variety of conditions. A little apatite is found in nearly all igneous rocks. It is common in pegmatite dikes and in contact-metamorphic deposits, and it is found also in veins, but in many lode ores it is not present, except in the wall rock. Apatite appears to be nearly insoluble in ascending thermal waters. The fresh and the altered wall rocks along lodes commonly show approximately the same amounts of apatite. Apatite is rare, though not unknown, as a

[1] Dudley, W. L., A curious occurrence of vivianite: Am. Jour. Sci., 3d ser., vol. 40, p. 120, 1890.

[2] Cross, Whitman, and Penrose, R. A. F., jr., Geology and mining industries of the Cripple Creek district, Colorado: U. S. Geol. Survey Sixteenth Ann. Rept., pt. 2, p. 129, 1895.

[3] Lindgren, Waldemar, and Ransome, F. L., Geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, p. 176, 1906.

[4] Sanford, Samuel, and Stone, R. W., Useful minerals of the United States: U. S. Geol. Survey Bull. 585, p. 11, 1914.

[5] Stose, G. W., Phosphorus ore at Holly Springs, Pa.: U. S. Geol. Survey Bull. 315, p. 474, 1907.

secondary mineral formed by surface decomposition. McCaughey[1] has obtained it by lixiviating a melt formed by dissolved calcium fluoride in fused sodium phosphate. Chlorapatite was made by adding calcium chloride to dicalcium phosphate, melting, and leaching with water.

Monazite, $(Ce,La,Di)PO_4$, and *xenotime*, $YtPO_4$, are rock-forming minerals and are found also in pegmatite veins.[2] Commercial supplies are obtained chiefly from placer deposits of sands derived from the mechanical disintegration of granitic gneisses and pegmatites.

Triphylite, $Li(Fe,Mn)PO_4$, and *amblygonite*, $AlPO_4LiF$, are known only as constituents of pegmatites and in veins of the deep zones, in which they are primary.

HALOIDS.

The principal haloids are stated below:

Calomel	HgCl.
Cerargyrite	AgCl.
Bromyrite	AgBr.
Iodyrite	AgI.
Atacamite	$Cu_2ClH_3O_3$.
Halite	NaCl.
Fluorite	CaF_2.
Cryolite	Na_3AlF_6.
Apatite	$(CaCl)Ca_4(PO_4)_3$.

The following table shows the solubilities of chlorine compounds in water at 18° C., determined by Kohlrausch:

KCl.	NaCl.	AgCl.	$BaCl_2$.	$SrCl_2$.	$CaCl_2$.	$MgCl_2$.	$ZnCl_2$.	$PbCl_2$.
329.5	358.6	0.0016	372.4	510.9	731.9	558.1	2,039.0	14.9
3.9	5.42	0.00001	1.7	3.0	5.4	5.1	9.2	0.05

The upper number in each square gives the number of grams of the anhydrous salt that is dissolved in a liter of water; the lower number is the molar solubility or the number of mols contained in a liter of the saturated solution.

As most of the metallic chlorides are highly soluble, they do not normally form in ore deposits. Silver chloride, which is relatively insoluble, is a common mineral. Lead chloride, which is only fairly soluble, is formed in small quantities. The silver haloids, all secondary, are discussed with the ores of silver. Fluorite is mainly primary, but some is secondary also. Apatite is primary. Common

[1] McCaughey, W. T., Jour. Phys. Chem., vol. 15, p. 464, 1911.

[2] Sterrett, D. B., Monazite deposits of the Carolinas: U. S. Geol. Survey Bull. 340, p. 272, 1908. Penfield, S. L., On the occurrence and composition of some American varieties of monazite: Am. Jour. Sci., 3d ser., vol. 24, p. 250, 1882.

salt (NaCl) is rare as a gangue mineral, but is abundant in the great copper deposits of Chuquicamata, Chile, and in the Boleo copper mines of Lower California. In deposits at Chuquicamata atacamite is a secondary mineral.

The solubilities of the fluorides at 18° C., also determined by Kohlrausch, are stated below:

KF.	NaF.	AgF.	BaF_2.	SrF_2.	CaF_2.	MgF_2.	ZnF_2.	PbF_2.
926.6 12.4	44.4 1.06	1,954.0 13.5	1.6 0.0092	0.12 .001	0.016 .0002	.076 .0014	0.05 0.0005	0.7 .003

The upper number in each square gives the number of grams of the anhydrous salt that is dissolved in a liter of water; the lower number is the molar solubility or the number of mols contained in a liter of the saturated solution.

These compounds, except calcium fluoride, are practically unknown as natural minerals, probably because the only common primary mineral, fluorite, is considerably less soluble than any other fluoride in the group, so that if any of the other fluorides were precipitated it would tend to go into solution again, the fluorite being precipitated. Other primary ores containing fluorine are cryolite and fluorapatite.

Fluorite, CaF_2, occurs in deposits of widely different character. It is a rock-making mineral in some granites and in other igneous rocks formed at depths; it occurs in some pegmatites and is found in veins formed at all depths. It is common in tin veins and in many gold and silver and some copper deposits.

At Cripple Creek fluorite is an abundant primary gangue mineral.[1] It is found also in ores of Georgetown, Rosita, Telluride, Rico, and many other districts in Colorado. A little is found in ores of the Florence vein, in the Judith Mountains, Mont., where it replaces limestone, and in the Hope mine, Philipsburg, Mont. It has been mined in the Burro Mountains, N. Mex. Considerable is present in lead ores at Silverbell, Ariz. At Ojo Caliente,[2] N. Mex., and at Wagon Wheel Gap, Colo.,[3] it is found near the surface in fissures, almost certainly in those from which hot springs now issue. The deposits at Wagon Wheel Gap are rather large and are now exploited.

It is produced in large quantity in southern Illinois,[4] where Mississippian beds are extensively faulted and intruded by lamprophyre dikes. Here veins in limestone, some of them nearly 40 feet

[1] Lindgren, Waldemar, and Ransome, F. L., The geology and gold deposits of the Cripple Creek district, Colorado: U. S. Geol. Survey Prof. Paper 54, pp. 122, 218, 1906.

[2] Lindgren, Waldemar, The hot springs of Ojo Caliente, N. Mex., and their deposits: Econ. Geology, vol. 5, p. 22, 1910.

[3] Emmons, W. H., and Larsen, E. S., The hot springs and the mineral deposits of Wagon Wheel Gap, Colo.: Econ. Geology, vol. 8, p. 242, 1913.

[4] Bain, H. F., Fluorite deposits of southern Illinois: U. S. Geol. Survey Bull. 255, 1905.

wide, are partly filled with fluorite, and some solid masses are 10 feet thick. A little galena, sphalerite, and some pyrite and chalcopyrite are associated with fluorite. The gangue minerals are quartz and calcite, and in some of the veins barite. Fluorite does not dissolve rapidly from the outcrops, and at some places the fluorite is recovered by placer mining. Fissure veins of fluorite are found also in Kentucky, where, according to Smith,[1] they mainly fill fissures and are not replacement veins. At the Riley mine, Crittenden County, Ky., fluorite ore fills a fault fissure between Carboniferous limestone and quartzite.

Fluorite is probably also a secondary mineral. Calcium fluoride, according to Wilson,[2] is soluble in water to the extent of about 37 parts per million at 16° C. Kohlrausch gives 16 parts in a million as the solubility at 18° C. Occurrences in geodes far removed from igneous activities indicate its origin in cold solutions. Nevertheless, observations of its occurrences as a secondary mineral in mines of sulphide ores are few indeed.

Cryolite, Na_3AlF_6, is a comparatively rare mineral. The principal deposits are at Ivigtut, in south Greenland, where a wide vein in granite[3] carries, with much cryolite, a little siderite, quartz, pyrite, chalcopyrite, and sphalerite. Peripheral phases of the vein carry also feldspar, cassiterite, fluorite, and other minerals. A cryolite quartz vein in granite is located south of Pikes Peak, Colo.[4]

[1] Smith, W. S. T., The lead, zinc, and fluorspar deposits of western Kentucky: U. S. Geol. Survey Prof. Paper 36, p. 142, 1905.

[2] Wilson, George, On the extent to which fluoride of calcium is soluble in water at 60° F.: British Assoc. Adv. Sci. Rept. Twentieth Meeting, pp. 12, 69, 1850.

[3] Quale, Paul, An account of the cryolite of Greenland: Smithsonian Inst. Rept., 1866, p. 398.

[4] Dana, J. D., System of mineralogy, 6th ed., p. 167, 1892.

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